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GAS ABSTRACTS

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I. GAS INDUSTRY

Canadian Gas

Ralph, H. D. CANADA GAS LINE NEARER. *Oil Gas J.*, **51**, 85, 86 (1952) October 20.

Now that Westcoast Transmission Co., Ltd. has the full approval of all Canadian authorities concerned and has proof of adequate reserves to support its pipeline, it is expected to ask for immediate resumption of hearings before the Federal Power Commission to construct a natural-gas pipeline from Northern Alberta and British Columbia to Vancouver, B. C., Seattle and other Washington cities. D. C. Gami

Explosion Liability

Parker, L. T. EXPLOSION LIABILITIES SUGGEST PRECAUTIONS FOR UTILITIES. *Am. Gas J.*, **177**, 18-19 (1952) October 1.

Court cases are cited to indicate to what degree and under what circumstances gas utilities are liable for gas explosions. Suggested precautions for avoiding liability are given.

E. J. Pyrcioch

Gas Costs and Prices

GAS INDUSTRY FEELS PRICE PINCH. *World Oil*, **135**, 83-86 (1952) October.

The gas industry as a whole is feeling painfully the impact of higher wages, higher costs of material and higher taxes. It is necessary to increase gas rates to earn a fair return and to operate on a sound economic basis. D C. Gami

Gas Industry Research

Bennett, C. E. GAS FACES ITS GREATEST CHALLENGE. *Am. Gas Assoc. Monthly*, **34**, 2-4 (1952) November: *Gas Age*, **110**, 39-44, 102 (1952) November 20.

An abridged version is given of the address to the opening session of the 1952 AGA Convention by the president of AGA. He outlines the pattern of the Gas Industry's phenomenal growth, and its needs to assure continued growth. He stresses the need for a greatly expanded research program under the PAR Plan. At present only $700,000 is allocated to research; that is one-fifth of one percent of the gas industry net revenue for 1951. He believes this budget should be materially increased.

A. E. Neumann

Zachry, C. H. RESEARCH PATTERN FOR PROGRESS. *Am. Gas Assoc. Monthly*, **34**, 13, 14, 46, 47 (1952), October.

After defining research the author discusses general aspects of industrial research such as risk in research, desirability of fundamental research, and methods of carrying out research, i. e. in company laboratories, by research agencies, or by cooperative research with others. The advantages of cooperative research for the gas industry are stressed. Next the research program sponsored by the Technical and Research Committee of the Natural Gas Department of the A.G.A. under the PAR plan is briefly outlined. The budget for this program is $88,500 for the current year and only 61 percent has been subscribed. It is stressed that this is a minute sum compared to the revenues of the pipeline companies, and it is suggested that consideration be given to increased support of the research program. O. T. Bloomer

GAS RESEARCH NEEDED. *Oil Gas J.*, **51**, 73-74 (1952) November 3.

This article summarizes several papers from the recent AGA convention. Although natural gas reserves indicate a supply for some years to come, one paper holds that the industry should sponsor studies on coal gasification with a view toward the time when the natural gas supply becomes inadequate. In a second paper the growth and economic attraction of the petrochemical industry is reviewed. J. D. Parent

Fuel Research

Hinshelwood, C. N. and Parker, A. FUEL RESEARCH 1951: REPORT OF THE FUEL RESEARCH BOARD. Dept. of Scientific and Industrial Research (H.M.S.O., London, 1952).

Research programs under way during the year are reviewed. Weakly-caking coals have been successfully blended for coke manufacture. Water gas has been produced by the fluidized solids technique on a small pilot-plant scale. A slagging cyclone generator has been built for suspension gasification of coke breeze. Extensive studies of the Fischer-Tropsch process are outlined, including properties and fluidization of catalysts, reaction-mechanism and properties of petroleum residuals. Work on physico-chemical techniques, boilers and steam-raising, sul-

fur removal from waste gas, gas turbines, domestic heating, and air pollution is discussed. Extension of the library, intelligence, abstract and publicity services is reported. A list of 20 publications is given. O. P. Brysch

Pipe Line Accounts

Interstate Commerce Commission UNIFORM SYSTEM OF ACCOUNTS FOR PIPE LINE COMPANIES (pp. 48 + iv, G.P.O.) Issue of 1952, revised to July 1, 1952.

This manual explains in detail the uniform system of accounts for pipeline companies prescribed by the Interstate Commerce Commission in accordance with section 20 of the I.C.C. act. J. D. Parent

State Regulations

Jones, B. STATE LEGISLATURES' ACTION ON UTILITY LAWS. *Public Utilities Fortn.*, 50, No. 8, 486-489 (1952) October 9.

New trends in gas industry regulation are discussed. Extension of the upward trend in rates will be accompanied by increased pressure for more stringent state regulation. The few state legislatures which met during this year devoted considerable attention to natural gas. In New England, New York and New Jersey, pipe line safety standards were a primary concern; restoring land to its "original condition" after the laying of pipe lines was the objective of Kentucky and Massachusetts legislation; Illinois and Nebraska approved underground storage. Developments in several states extended the trend toward broader regulation of liquefied petroleum gas sales. A. E. Neumann

2. APPLIANCES

Gas Burners

Connors, J. D. COMBUSTION FOR GAS CONVERSION BURNERS. *Heating Ventilating*, 49, 83-87 (1952) October.

Discussion is given of the influence of various design and installation factors on the proper combustion of gas for greatest heating efficiency. Data are included for guidance in the selection of the proper type of gas conversion burner. Author's Abstract

Gas Burners

Downe, E. R. (assigned to C. A. Olsen Manufacturing Co.) FLAME RETAINING ATMOSPHERIC GAS BURNER. U.S. 2,610,675 (1952) September 16.

A flame-retaining gas burner is described. E. F. Searight

Taylor, R. S. (assigned to Servel, Inc.) GAS RANGE. U.S. 2,611,358 (1952) September 23.

A gas range with provisions for venting the top burners is described. E. F. Searight

Ignition

Eskin, S. G. (assigned to Robertshaw-Fulton Controls Co.) ELECTRIC IGNITION AND AUTOMATIC PILOT FOR GASEOUS FUEL BURNERS. U.S. 2,614,622 (1952) October 21.

An electric ignition system for gas burners is described. E. F. Searight

3. COMBUSTION AND INDUSTRIAL FURNACES

Carburizing

GAS CARBURIZING. *Ind. Finishing* (British), 5, 217-219 (1952) October.

A process for preparing town gas for use in gas carburizing is discussed. E. F. Searight

Gas Turbines

Burris, R. E. and Hatch, B. G. HOW G. E. TESTS GAS TURBINES. *Power Eng.*, 56, 62-65 (1952) October.

An account is given of the procedures and the facilities required for testing gas turbines before they are shipped to the purchaser. This reduces the shakedown period for testing and adjustments on the purchasers installation but requires a large investment in the manufacturers test-stand facilities. E. J. Pyrcioch

Hague, F. T. THE PATTERN OF GAS-TURBINE DEVELOPMENT IN EUROPE AND THE UNITED STATES. *Mech. Eng.*, 74, 627-632 (1952) August.

A review of gas-turbine development in Switzerland, England, and the United States since the late thirties is given. Recent work on gas-

turbine power generating units, marine plants and aviation turbines is described. A discussion on the use of residual-oil and natural gas as fuel for gas turbines is presented. The largest coal-burning gas-turbine research project covers the development of a plant for locomotive use. Only one gas turbine for pumping natural gas through pipe lines has been in actual extended operation although a large number have been sold for this purpose. E. J. Pyrcioch

Submersible Burner

Swindin, N. SUBMERSIBLE BURNER. U.S. 2,611,362 (1952) September 23.

A submersion burner for use in pickling of iron and steel is described. E. F. Searight

4. CARBONIZATION AND GASIFICATION

Butane-Air Gas

Cosby, W. T. THE USE OF BUTANE IN SMALL GAS WORKS. *Gas World*, 86, 703-709 (1952) September 20.

A comprehensive description of equipment and installations of a standard butane-air plant in a typical English town is given. A short analysis of combustion properties and appliance conversion for the butane-air system is included. W. G. Bair

Coal Cleaning

Needham, L. W. THE CLEANING OF SMALL COAL—II. *Gas World* (British), 86, Coking Section, 39-46 (1952) September 6.

Jigs, trough washers and the Dutch cyclone are discussed in some detail. Jig washers of the Baum type are used to a major extent in Britain for cleaning coking coal slacks. The influence of the size of particle upon the specific gravity of separation (for 50% yield), and therefore upon the performance of jigs and troughs, is explained. High middlings content requires this specific gravity to be kept low. Specially designed jigs, and separation of slack into 2 size fractions have been successful with high-middlings coals. Ground shale or magnetite suspensions in the cyclone washer have been useful for small coal down to 0.5 mm., but require complicated apparatus for reclaiming the medium. For finer coal particles the flotation process is attractive. Dewatering of the cleaned coal is about as important as cleaning, and methods and costs are discussed. (See *Gas Abs.* 8, 208 (1952) November for Part I). O. P. Brysch

Coal Free-Swelling Index

Shotts, R. Q. INFLUENCE OF CERTAIN INORGANIC MATTER, FUSAIN AND "DULL" COAL ON THE FREE SWELLING INDEX OF COAL. *Fuel* (British) 31, 448-461 (1952) October.

The effects on the free swelling index of several coals, of dilution with varying quantities of high density fractions of the coals, quartz, shale, ignited shale, fusain, vanadium pentoxide, ammonium chloride and boron oxide are studied. Inorganic diluents had little effect, up to 30 per cent inorganic matter. Organic materials decreased free swelling somewhat more rapidly, fusain-rich dust being the most effective substance tried. Moderate quantities of vanadium pentoxide and ammonium chloride had little effect upon strongly swelling coals but reduced noticeably the swelling of coals having lower indexes. Boron oxide lowered free swelling effectively, even for strongly swelling coals. No evidence was found that the gross quantity of volatile matter in the mixtures greatly affected swelling. Author's Abstract

Coal Oxidation Chemistry

Franke, N. W., Kiebler, M. W., Ruof, C. H., Savich, T. R., and Howard, H. C. WATER-SOLUBLE POLYCARBOXYLIC ACIDS BY OXIDATION OF COAL. *Ind. Eng. Chem.*, 44, 2784-2792 (1952) November.

A review is given of the Carnegie Coal Research Laboratory work on oxidation of coals to organic acids, with special emphasis on operations of a 25-gal. pilot plant. Pocahontas coal and 500° coke were found to give highest yields of organic acids (50%). Fifteen-lb. charges of -100 mesh coal in strong sodium hydroxide solution were oxidized at 270° C. and 900 psig with oxygen gas. Nature and yields of products and their possible uses are treated in some detail. About one-third of the acid yield is a benzene-carboxylic acid fraction, useful in plasticizers, resins, lubricants, metal cleaners or emulsion breakers, largely as a replacement for phthalic acid. Commercialization costs for the process are discussed. O. P. Brysch

Coal Pyrolysis

Frien, C. H. PYROLYSIS OF COAL AND SHALE. *Ind. Eng. Chem.*, 44, 2064-2072 (1952) September.

Papers on coal pyrolysis during the past year have included discussions of the colloidal structure of coal, mechanism of swelling, function of the polar atoms present, and the kinetics of decomposition. The preparation of suitable blends for the oven and the effect of pulverization on coking have been noted. Fluidized bed coking and underground electrocarbonization are described, as is also pyrolysis by dielectric means. Catalytic action of sodium compounds during low-temperature carbonization and a rapid semicoking process employing superheated steam are mentioned. The substitution of calcium sulfate for acid in ammonia recovery is proposed, as is ethylene recovery by selective solvent absorption. New methods of analysis for phosphorus have been devised. Underground gasification with oxygen has been suggested as a substitute for the Ljungstrom electrocarbonization of shale in Sweden. Little new research on the fundamental chemical nature of kerogen has been published. A fluidized vacuum-retorting study, research on low-temperature depolymerization in the presence of solvents, and an excellent paper on the role of nitrogen in shale-oil hydrocarbon formation have been reported. A three-stage fluidization process of retorting has been patented. Hydrogenation studies on Colorado shale oil have been completed. A survey of methods of nitrogen determination in shale oil fractions has been conducted. Author's Abstract

Coke Oven Machinery

Lavely, P. H. (assigned to Koppers Company, Inc.) PUSHER MACHINE WITH ARTICULATED PUSHER BAR. U.S. 2,609,948 (1952) September 9.

An improved coke-oven pusher ram is claimed, in which the length of the ram is reduced by a hinged joint, automatically actuated when the ram is retracted. O. P. Brysch

Lavely, P. H. (assigned to Koppers Co., Inc.) LEVELER BAR AND RECIPROCABLE FRAME. U.S. 2,609,949 (1952) September 9.

An improvement in coke-oven charge levelers is shown in which the supporting bearing structure for the reciprocating leveler-bar can be moved forward to a point near the leveling-door, to provide increased stability and control for the bar. O. P. Brysch

Experimental Oven

Gayle, J. B. and Auvil, H. S. DEVELOPMENT OF NEW EXPERIMENTAL COKE OVEN. U.S. Bureau Mines Report of Investigations 4923 (1952) October.

This report describes in detail the "Tuscaloosa" test-oven, designed to duplicate commercial slot-oven conditions. The unit is 17 in. wide, 30 in. long and 48 in. high with 4½ in. silica-brick walls and zoned heat input (Globars). A suspended wall is held against the chamber structure by 2 top and 2 bottom tie-tubes, each carrying a ring-type, accordion-pleated hydraulic gland which bears against a bracket on the moveable wall. Each gland registers on a Bourdon gage, the four permitting tests up to pressures of 10 psi. Vertically-moveable doors permit mechanical pushing of charge; coal preparation, storage and charging equipment are provided. Operating results of 2 years are discussed. Standby temperatures of 1500° F. require 17 kwh/hr and operating temperatures of 2600° F. require 47 kwh/hr; a 65-kva transformer suffices to supply the 3 (bottom, top and middle) horizontal Globar groups of each wall, and the 4 separate vertical Globars at each corner. No difficulty has been encountered with the silica brick. Duplicate oven tests gave coke with closely-agreeing properties. Also the test-oven coke was in agreement with commercial oven coke in shatter, tumbler and sp. gr., but on screen-tests, the former is larger. Research on coking time, pressures, temperature progression, coal moisture and test-apparatus comparisons are planned. O. P. Brysch

Germanium Content

Aubrey, K. V. GERMANIUM IN BRITISH COALS. *Fuel* (British) 31, 429-437 (1952) October.

The germanium contents of some 200 British coals from all the main coalfields have been determined by spectrographic analysis of the ashes. The average germanium content of these coals, about 7 ppm. is of the same order as the content of most sedimentary rocks. Apart from the coals derived from the South Wales coalfield tending to have low germanium contents, there

is no evidence of a marked regional variation in average germanium content. The bulk of the germanium in British coals appears to be present in intimate association with the organic matter of the coal rather than with the adventitious mineral matter. Author's Abstract

Humic Acid Research

Polansky, T. S. and Kinney, C. R. MOLECULAR WEIGHTS OF HUMIC ACIDS PREPARED FROM NITRIC ACID TREATED BITUMINOUS COAL. *Fuel* (British) 31, 409-413 (1952) October.

Nitric acid-treated coal extracted by 90% acetone gave a yield of 85.1% of humic acids which represented 70.7% of the C of the original coal. Cryoscopic molecular weight studies using catechol and acetamide as solvents gave corrected values of 279 and 642 respectively. With dry acetone and with dioxan-water azeotrope, 584 and 285 were obtained. The variability indicates that strongly associated substances are present, and since catechol and dioxan-water results show dissociation to less than twice the equivalent weight of these acids, at least some of the molecules therefore are monobasic. The strong associating forces may be explained by the presence of nuclear structure similar to the carbon structures in carbon blacks.

O. P. Brysch

Plant Waste Treatment

Biehl, J. A. CUT PHENOLS IN WASTE BY 99.9%. *Petroleum Processing*, 7, 1435-1437 (1952) October.

This article claims the development of a process to reduce the concentration of phenol in aqueous solutions from 200 ppm. to 0.2 ppm. No full-scale unit has yet been built although the flow diagram for a proposed unit is given. Laboratory data are reported. Graphs are presented, showing the solubilities of the solvent constituents in water versus temperature, and % phenol removed versus % aromatics in solvent with parameters of solvent-to-waste ratios. As expected, the % phenol removed increased as the ratio of solvent-to-waste increased and as the % aromatics in the solvent increased. However, practical considerations regarding solvent regeneration and solvent loss limit the independence of these variables. J. I. Wrozina

Coe, R. H. BENCH-SCALE METHOD FOR TREATING WASTE BY ACTIVATED SLUDGE. *Petroleum Processing*, 7, 1128-1132 (1952) August.

This article discusses the action of activated sludge in a continuous bench-scale set-up on the elimination of refinery effluent contamination. The following factors were varied and the results noted: the pH of the feed stock, the amounts of phenols, salts, solid material, and sulfides in the feed stock. The aeration time was varied, as was the residence time. Two tables are presented, showing: (1) the effect of loading on effectiveness of treatment, and (2) the effect of preaeration followed by bio-treatment. J. I. Wrozina

Reforming Hydrocarbons

Pollock, L. W. (assigned to Phillips Petroleum Co.) PRODUCTION OF FUEL GAS BY CRACKING PROPANE. U.S. 2,608,478 (1952) August 26.

A process is claimed for the production of a fuel gas having a 500 to 700 Btu./cu.ft. range by cracking hydrocarbon gas rich in propane at temperatures from 1650° to 2200° F. The temperature is obtained by heated pebbles passing through the reaction zone. The pressure is maintained at 1 and 2 atmospheres, the steam to propane molar ratio at about 2, and the contact time at about 0.7 seconds.

H. A. Dirksen

Webb, G. M. and Moehl, R. W. (assigned to Universal Oil Products Co.) HYDROCARBON CONVERSION CATALYST AND PROCESS. U.S. 2,611,738 (1952) September 23.

An improvement is claimed in the manufacture of a silica-metal oxide catalyst, which compresses the composite of silica hydrogel and metal oxide at 100° F. to 250° F. for at least an hour in an ammonium salt solution with a pH below 9. The amount of fines normally encountered in the catalyst preparation is reduced.

H. A. Dirksen

The following articles, the abstracts for which appear on the pages indicated, are also called to your attention:

Ingles, O. G. WATER GAS SHIFT REACTION. p. 237

Kinney, I. W., Jr. IDENTIFICATION OF THIOPHENE AND BENZENE HOMOLOGS. p. 234

Vahrman, M. ASPECTS OF CHEMISTRY OF COAL TARS. p. 237

5. NATURAL GAS AND NATURAL GAS CONDENSATES

British LP-Gas

Edwards, E. M. DEVELOPMENTS IN THE USE OF LIQUEFIED PETROLEUM GASES. *Gas World* (British), 136, 841-846 (1952) October 4; *Gas J.* (British) 272, 96-102, 107, 111, 116 (1952) October 8; *Gas Times* (British) 73, 24, 25-28, 33 (1952) October 3.

With the problem in mind of the gas supply of the smaller isolated communities of Wales, the Wales Gas Board installed an experimental LP-gas/air station at Whitland. This consisted of one French (Mallet) and one American (Gasair) plant. Developments reported are concerned with (a) calorific value (b) load survey (c) gas-air mixtures (d) appliance conversion (e) changeover (f) plant description and installation (g) results (h) costs, (i) design (j) conclusions. Utilization has been treated in some detail. O. P. Brysch

Condensate Recovery

Stormont, D. H. AUTOMATIC CONDENSATE COLLECTORS FEATURE ELK HILLS SYSTEM. *Oil Gas J.*, 51, 192-194 (1952) October 13.

The 100-mile gathering system is provided with 93 automatic drip collectors. The construction and operation of mainline collectors are discussed. I. P. Patel

Distribution

Crilly, J. J. SINGLE CONTROL ROOM INTEGRATES ENTIRE SYSTEM. *Gas*, 28, 53 (1952) October.

The central control system used by Elizabethtown Consolidated Gas Company to control natural gas dispatching operation to the Elizabeth, N. J. area is discussed. E. F. Searight

Hanna, L. G. SAFE PRACTICES IN DISTRIBUTION OF NATURAL GAS. *Am. Gas J.*, 177, 17, 30 (1952) September.

The use of dresser-type couplings is recommended instead of collars on service lines and outside meter sets. Meters should be installed above ground outside buildings. In the main lines, welded construction should be used. I. P. Patel

Gas Engine vs Turbine Pumps

Haverfield, F. B. STEAM CENTRIFUGAL COMPRESSORS. *Pipe Line News*, 24, 45, 46-54 (1952) October.

Transcontinental Gas Pipe Line Co. is employing three steam-turbine-driven centrifugal compressor stations along with sixteen gas-engine-driven stations in the main line and each steam station has three 5000 hp. units which are operated in series. A brief description of the plants is given along with some comparitive operating and personnel requirement data. The centrifugal stations were cheaper by $45.00 per installed horsepower than the equivalent gas-engine-driven stations. This was due to elimination of massive foundations and to use of smaller buildings. The operating costs were 0.16 cents for the steam station and 0.186 cents for the gas-engine driven station. O. T. Bloomer

Sterrett, E. STEAM TURBINE DRIVE FOR MAIN LINE COMPRESSORS. *Pipe Line News*, 24, 47-54 (1952) October.

This article presents a rather complete description of steam centrifugal compressor stations. The article is illustrated with many photographs. O. T. Bloomer

Gasoline Recovery

Barry, C. B. PORTABLE GASOLINE PLANTS GAIN IN POPULARITY. *Oil Gas J.*, 51, 96-98, 106 (1952) October 27.

A skid-mounted packaged gasoline plant is described and advocated for minimum risk prior to erection of a major plant. A standard unit would process about 5 MMCF/day and would employ the oil absorption process, using an absorber pressure of 150 psi and an oil of 180 molecular weight circulated at 25 gallons/min. Rich oil is flashed, the liquid phase heated and sent to a dry still where flashed vapor rather than open steam is used for stripping. Only 90 to 95% of the pentanes is recovered and no gasoline separation is proposed although LPG production is possible. The accent is placed on simplicity and safety to minimize operating expense. J. D. Parent

H_2S Removal

Atcheson, M. and Cohn, A. A. OPERATING GLYCOL-AMINE GAS TREATING PLANTS. *World Oil*, 135, 297-300 (1952) October.

Remedial measures for operating problems of

the glycol-amine process are discussed. These problems include the corrosion of solution exchangers and stills, the reduction of contactor capacity by accumulated corrosion products in the bubble cap, and the deterioration and loss of glycol-amine solution. C. E. Hummel

LP-Gas

Coumbe, A. T. and Avery, I. F. LP-GAS DOES IT AGAIN: 21 PER CENT SALES GAIN IN '51. *LP-Gas*, **12**, 44-47 (1952) September.

Sales of propane, butane and mixed propane and butane are given for the period 1946 through 1951. Amounts consumed are broken down into the usual groups such domestic, chemical, gas manufacture, etc. and a 21.4% sales gain over the previous year is noted. Geographical distribution of sales during 1950 and 1951 is given in detail. J. D. Parent

Turner, C. C. THE BULK PLANT. *LP-Gas*, **12**, 58-79 (1952) October.

This lengthy discussion presents the economics of bulk plants. Some cost data plant layout and operating information is included.

J. D. Parent

L-P Power Market

THE POWER MARKET. *Butane-Propane*, **14**, 104-116 (1952) September.

A discussion of the application of LP-fuel in the internal-combustion engine market is given. Mass sales to truck and bus lines, heavy construction equipment and tractors are much preferred to individual passenger car sales.

W. G. Bair

Pipeline Construction

Watkins, E. G. DESIGN OF GAS PIPING ON BRIDGES. *Gas*, **28**, 53-62 (1952) September.

Keeping the stresses in the pipe within tolerable limits is of utmost importance when installing gas mains on bridges. Methods for accommodating stresses induced by expansion and contraction are discussed, including the use of expansion joints, pipe loops, roller supports, and anchorage to the bridge. Ordinarily, no elaborate construction is required for either support or expansion of low-pressure lines on bridges. Only when a combination of temperature range, span and operating pressure reach limits of tolerable stresses must consideration be given to stricter methods of installation.

E. J. Pyrcioch

Production

Humason, G. A. GAS LIFT. U.S. 2,612,111 (1952) September 30.

The invention relates to equipment for raising oil or other fluid from a well part way by injected gas so it can then be handled by the pumping string. J. D. Parent

Little, H. E. GAS WELLS FROM DEPLETED OIL WELLS. *World Oil*, **135**, 262, 270 (1952) October.

Increased gas production is being obtained in the Permian Basin by re-completing oil wells produced beyond their economic limit. The practice is due to the increase in price and demand for gas. Wells are plugged back and the casing is perforated opposite other strata. Radioactive well-logging is used to help locate possible strata where well records are incomplete. O. T. Bloomer

Transcontinental's Line

Hangs, F. E. HIGHLIGHTS IN TRANSCONTINENTAL'S CONSTRUCTION PROGRAM. *Pipe Line News*, **24**, 34-44 (1952) October.

A brief history together with the detail of design and construction of 1840 miles of 30" pipe line of Transcontinental Gas Pipe Line Corp. is given. Design features include a maximum line pressure 800 psi, with a compression ratio of 1.4; pipe-wall thickness is 0.3125" to 0.500" depending on outside conditions. The application of steam-driven centrifugal compressors at three stations is new in the field.

D. C. Gami

Underground Storage

Brown, C. B. OAKFORD PROJECT WILL STORE 105 BILLION CUBIC FEET OF GAS. *Oil Gas J.*, **51**, 102-106 (1952) October 27.

Process details for the huge Oakford Storage Project near Jeanette, Pa. are given. Total capacity is 105,000 MMCF of which 60,000 MMCF may be withdrawn. Compression facilities total 30,000 hp. and gas can be dehydrated both before injection and after removal. Two sand strata are to be used. Five years will be required before the joint operators, Texas Eastern and New York State Natural, have the project at full capacity. J. D. Parent

Oates, J. F., Jr. UNDERGROUND STORAGE OF NATURAL GAS: ITS THEORY AND PRACTICE. *Gas Age*, **110**, 23-24, 69-73 (1952) October 9.

The author reviews the search made by his company for adequate underground storage. Geological and economic considerations relevant to the various solutions which were possible, are reviewed and the reasons for selecting the Herscher dome aquifer are given. Steps taken in the development of the project are presented. J. D. Parent

The following articles, the abstracts for which appear on the pages indicated, are also called to your attention:

Barker, C. L. COMPUTING FLOW CONDITIONS IN GAS LINES. p. 239

Haupt, L. M. PIPE LINE FLUID NETWORK CALCULATOR. p. 239

Mellen, G. L. VELOCITY METERING OF GAS FLOW. p. 239

6. PETROLEUM AND SYNTHETIC LIQUID FUELS

Canadian Oil

Menneer, J. CANADIAN OIL PANORAMA. *Petroleum Eng.*, **24**, A45-A58 (1952) October.

The geological features of the Western Canada Basin are presented and the exploration and economic development traced, particularly for the last 5 years. Reserves data for oil and gas are given. J. D. Parent

Composition of Crudes

Smith, H. M. COMPOSITION OF UNITED STATES CRUDE OILS. *Ind. Eng. Chem.*, **44**, 2577-2585 (1952) November.

The crude oil-producing areas of the United States are divided into eight geographical areas. Certain characteristics of the crude oils produced in each area are discussed in this paper. Characteristics, based on the Bureau of Mines routine analysis, include the sulfur, asphalt, naphtha, gas oil, aromatics in both the naphthas and gas oils, and naphthene ring in the paraffin-naphthene portions of both the naphthas and the gas oils. A total of 330 crude oils is included in the discussion. Author's Abstract

Conversion Catalysts

Browning, L. C. and Emmett, P. H. EQUILIBRIUM MEASUREMENTS IN THE Mo-C-H SYSTEM. *J. Am. Chem. Soc.*, **74**, 4773-4872 (1952) October 5.

The equilibrium data for the temperature range studied show Mo_2C and MoC are thermodynamically stable with respect to molybdenum and carbon. Equilibrium data for the reaction $2\ Mo + CH_4 = Mo_2C + 2H_2$ and $Mo_2C + CH_4 = 2\ Mo\ C + 2H_2$ were obtained and confirmed by x-ray spectrogram for the temperature range 447-682° and 663-825° respectively.

H. A. Dirksen

Fischer-Tropsch Process

Clark, A. (assigned to Phillips Petroleum Co.) SYNTHESIS OF HYDROCARBONS. U.S. 2,610,200 (1952) September 9.

A process is claimed for synthesizing hydrocarbons from a suitable mixture of hydrogen and carbon monoxide passed over a cobalt catalyst at from 175 to 225° C. and 5 to 150 atmospheres, using a two-stage arrangement with the introduction of fresh carbon monoxide to the scrubbed gas before the gas enters the second stage reactor. W. J. Pleticka

Ghosh, J. C., Sastri, M. V. C., and Kini, K. A. ADSORPTION OF HYDROGEN AND CARBON MONOXIDE AND THEIR MIXTURES BY COBALT FISCHER-TROPSCH CATALYSTS. *Ind. Eng. Chem.*, **44**, 2463-2470 (1952) October.

Two cobalt Fischer-Tropsch catalysts were used to obtain adsorption data of pure carbon monoxide and hydrogen, and of mixtures of the synthetic gas ($1CO: 1H_2$ and $1CO: 2H_2$). Kinetic and adsorption data are presented with graphs for each catalyst and mixture. The adsorption data combined the conversion and yield data of the two catalysts, and indicates a final ratio of $2CO: 1H_2$ corresponding to a complex of the enolic formula (-C-O-H) as the intermediate product. H. A. Dirksen

Moran, J. N. (assigned to Phillips Petroleum Co.) PROCESS FOR THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN BY MEANS OF A FLUIDIZED FIXED-BED. U.S. 2,612,512 (1952) September 30.

A fluidized fixed-bed method for synthesizing

hydrocarbons by reacting hydrogen and carbon monoxide is claimed. W. J. Pleticka

Owen, J. J. and Sumerford, S. D. (assigned to Standard Oil Development Co.) PROCESS FOR THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN WITH AN IRON TYPE CATALYST. U.S. 2,610,975 (1952) September 16.

This invention refers to the method of increasing the content of high molecular weight hydrocarbons in the total liquid product synthesized from carbon monoxide and hydrogen, by controlling the oxygen content of iron catalyst in a fluidized synthesis reactor.

C. von Fredersdorff

Rubin, LC., Riblett, E. W., McGrath, H. G. (assigned to M. W. Kellogg Co.) SYNTHESIS OF ORGANIC COMPOUNDS. U.S. 2,615,035 (1952) October 21.

The patent claims improved liquid hydrocarbon recovery by using catalyst temperatures between 440° F. and 500° F., a space velocity of approximately 1000, and pressures from atmospheric to 45 psi. The conversion of carbon monoxide is maintained above 50% p/h over the fluidized cobalt catalyst. The synthesis gas varied in composition from 2:1 to 5:1 mol. ratio hydrogen to carbon monoxide.

H. A. Dirksen

Incentives

Fell, H. B. INDIVIDUAL FREEDOM VERSUS STATISM IN PETROLEUM. *Independent Petroleum Assoc. of America*, 23, 57-58 (1952) October.

History shows that captive peoples produce inferior goods and in lesser amounts than those who are allowed profit incentives. Examples are given from the petroleum producing field.

J. D. Parent

Synthesis Gas

Stewart, S. G. (assigned to Phillips Petroleum Co.) SYNTHESIS GAS MANUFACTURE. U.S. 2,606,158 (1952) August 5.

The patent claims the manufacture of a hydrogen, carbon monoxide synthesis gas with a 1.7:1 to 2.3:1 hydrogen ratio by passing C_1 to C_4 hydrocarbon with oxygen through a reactor at 2000 to 2500° F. with a residence time of 0.02 to 2 seconds for partial oxidation, and quenching the products rapidly to prevent the water-gas shift from taking place. The heat released in the quenching operation is used for thermal cracking of the charging stock.

H. A. Dirksen

Shale Oil

Cheney, L. K. (assigned to Sinclair Refining Co.) PYROLYTIC CONVERSION OF OIL SHALE. U.S. 2,609,331 (1952) September 2.

The addition of from 0.5 to 6% of hydrochloric or hydrofluoric acid to a slurry of oil shale produces an active catalyst by reacting with the inorganic constituents in the shale thereby catalyzing the shale oil production in the retorting operation. E. J. Pyrcioch

7. ANALYTICAL METHODS AND TESTS

Adsorption Analysis

Spengler, G. and Krenkler, K. SELECTIVE ADSORPTION OF HYDROCARBONS. *Petroleum Refiner*, 31, 133-136 (1952) October.

Work in Germany on hydrocarbon analysis of gasoline by percolation through silica gel and activated charcoal is described. The method consisted of percolation of a mixture of gasoline and n-hexane throngh a small column of the adsorbent until the original mixture began to appear; no developer other than the sample mixture was used. Characteristic curves for different gasoline types were observed, but a strictly quantitative method for hydrocarbon types apparently was not achieved.

D. M. Mason

Coal Ash Method

Tomlinson, R. C. and Edwards, A. H. A TEST TO DETERMINE THE EFFECT OF DIFFERENT SIZED DISHES IN ASH DETERMINATION. *Fuel*, (British) 31, 468-474 (1952) October.

A test is described which was designed to determine the difference in the results of ash determinations when two kinds of dishes were used. The work is of interest as an example of a simple experiment statistically designed so as to obtain the answers to specific questions

with a minimum of work. The tests, which were carried out in Newcastle Coal Survey Laboratory, showed that the use of a smaller flangeless dish (49 mm internal diameter) gave results slightly higher than those obtained with a larger flanged dish (57 mm internal diameter). The difference was small, between 0.01 and 0.11, and the accuracy of the determination was the same in both cases. Authors' Abstract

Cyanide Determination

Fisher, F. B. and Brown, J. S. COLORIMETRIC DETERMINATION OF CYANIDE IN STACK GAS AND WASTE WATER. *Anal. Chem.*, **24**, 1440-1444, (1952) September.

A method, which is based on the reduction of sodium picrate by cyanide to form a colored product, is presented for the quantitative determination of cyanogen and hydrogen cyanide in refinery stack gases and of those cyanides in refinery waste matters which are readily decomposed by strong acids. The determination is sensitive to 1 p.p.m. and accurate to within 2% of the correct value; the developed color is stable and the determination is not affected by the other substances normally encountered in refinery wastes. The paper presents a comprehensive discussion of the variables affecting the picrate-cyanide reaction, such as reaction rate, reagent concentration, color stability, and interfering substances. Authors' Abstract

Mass Spectrometry

Kinney, I. W., Jr. and Cook, G. L. IDENTIFICATION OF THIOPHENE AND BENZENE HOMOLOGS. *Anal. Chem.*, **24**, 1391-1396 (1952) September.

A new method for the identification of unknown organic compounds has been developed, using correlations that relate mass spectra with molecular structure. No prior mass spectral data for the unknown compounds are necessary for identifications. The basis of the method is the use of mass spectral correlations to identify structural groups in unknown compounds. Identifications are completed by the use of supplemental chemical and physical data.

Authors' Abstract

Lumpkin, H. E., Thomas, B. W. and Elliott, A. MODIFIED METHOD FOR HYDROCARBON TYPE ANALYSIS BY MASS SPECTROSCOPY. *Anal. Chem.*, **24**, 1389-1391 (1952) September.

The mass spectrometer compound-type analysis developed by Brown is modified for application to samples of low olefin content. Paraffins, naphthalenes, aromatics, and condensed-ring naphthenes are determined in a single mass spectrometer run by the abundance of specific groups of peaks which are distinctive for the various compound types. The four types can be determined in olefin-free samples in 1 hour with an accuracy of about ± 10% of the amount of each type present.

Authors' Abstract

Sobcov, H. ANALYSIS OF LIQUID HYDROCARBON MIXTURES BY MASS SPECTROMETRY. *Anal. Chem.*, **24**, 1386-1388 (1952) September.

An investigation was made of the means by which rapid and accurate mass spectrometer analyses could be obtained for hydrocarbon mixtures boiling between 82° and 231° F. (isopentane to toluene). The problems of mass spectrometer reproducibility and close spectral similarities require fractionation of the sample by distillation. Thus far the smallest number of fractions required is four and the largest matrix deemed useful has been of fifteenth order.

Author's Abstract

Specific Surface

Rose, H. E. THE PERMEABILITY METHOD OF SPECIFIC SURFACE DETERMINATION. A CORRECTION FACTOR. *J. Applied Chem.* (British) **2**, 511-520 (1952) September.

In determination of specific surface of powders by the permeability method, a correction based on the effect of tortuosity of passages has been found which eliminates the effect of porosity of the bed. The values of specific surface obtained by this method deviate from values obtained by the application of the photo-extinction and nitrogen adsorption techniques by amounts which would be predicted from the known limitations of the alternative methods.

D. M. Mason

Spectroscopy

Pagliassotti, J. P. and Porsche, F. W. SPECTROSCOPIC DETERMINATION OF MET-

ALS IN SILICA-ALUMINA CRACKING CATALYSTS. *Anal. Chem.*, **24**, 1403-1405 (1952) September.

Unsatisfactory results with chemical analysis and insufficient aid given by silicon as internal standard in the spectroscopic determination of metals have led the authors to a method of dissolving the catalyst in hydrofluoric acid, with cobalt added as the internal standard, and obtaining the spectra by means of solution-excitation. Details are given for the analytical procedure. S. Sensi

Shale Oil

Cady, W. E. and Seelig, H. S. COMPOSITION OF SHALE OIL. *Ind. Eng. Chem.*, **44**, 2636-2641 (1952) November.

The ultimate analysis, the physical properties and a detailed breakdown into the various classes of hydrocarbons are given for a typical Colorado shale oil. H. R. Linden

SO_2 Determination

Patterson, G. D., Jr. and Mellon, M. G. DETERMINATION OF SULFUR DIOXIDE BY COLOR-CHANGING GELS. *Anal. Chem.*, **24**, 1586-1590 (1952) October.

Atmospheric sulfur dioxide is determined by drawing 150 ml. air samples over silica gel coated with ammonium vanadate or other inorganic or organic compounds. A change of color is produced by the presence of 10 p.p.m. or more of sulfur dioxide and the concentration is quantitatively estimated by matching the color with standard color cards. A summary is given of colorimetric-gel methods for analyzing other gases and vapors. C. E. Hummel

The following articles, the abstracts for which appear on the pages indicated, are also called to your attention:

Aubrey, K. V. GERMANIUM IN BRITISH COALS. p. 238

Cannon, C. G. INFRARED SPECTRA OF SOME AROMATIC COMPOUNDS. p. 237

8. GENERAL AND PHYSICAL CHEMISTRY

Combustion Reactions

Broida, H. P. and Lalos, G. T. ROTATIONAL TEMPERATURES OF *OH* IN SEVERAL FLAMES. *J. Chem. Physics*, **20**, 1466-1471 (1952) September.

The intensity of OH emission from various small regions of Bunsen-type flames of hydrogen, acetylene, methane, and propane, premixed with oxygen, has been observed spectroscopically, and corresponding rotational temperatures have been determined by an iso-intensity method. An ultraviolet grating monochromator of high resolution was used; fuel to oxygen ratios were varied from about 0.5 to 2 times the stoichiometric value; and rotational temperatures were determined at several positions within each flame. The measured temperatures of the reaction zone varied little with mixture ratio for a given fuel and were greater than adiabatic, suggesting a lack of thermal equilibrium. In the hot gases beyond the reaction zone, however, evidence was found of both rotational and electronic equilibrium. The concentration of thermally-produced OH in the burned gases was found to be so great that it tends to mask the emission from the reaction zone. Authors' Abstract

Shuler, K. E. and Broida, H. P. KINETICS OF *OH* RADICALS FROM FLAME EMISSION SPECTRA V. A STUDY OF THE ACETYLENE-OXYGEN FLAME. *J. Chem. Physics*, **20**, 1383-1388 (1952) September.

The inner cone of the acetylene-oxygen flame burning lean (1:5), stoichiometric (2:5), and rich (4:5) at atmospheric pressure has been studied spectroscopically with the object of gaining some information about the elementary processes occurring in this flame. The rotational, vibrational, and electronic distributions of OH ($^2\Sigma^+$) have been determined for each fuel mixture. The analysis of the data showed a rotational Maxwell-Boltzmann distribution with a rotational "temperature" several hundred degrees higher than the adiabatic flame temperature. The vibrational distribution of OH ($^2\Sigma^+$) was distinctly nonequilibrium with an excess population in the level $v' = 3$ anal-

ogous to that observed for the hydrogen-oxygen flame. This is attributed to the interaction of the ($^2\Sigma^+$) states of OH. The analysis of the electronic distribution of OH indicated that OH ($^2\Sigma^+$) is present in its thermal equilibrium concentration in the flame at atmospheric pressure. The results of this study in conjunction with the work of Gaydon and Wolfhard on the low pressure acetylene-oxygen flame indicate that the radiation of OH ($^2\Sigma^+$) is to a large extent chemiluminescence so that a considerable fraction of the excited hydroxyl radicals must have been formed in the ($^2\Sigma^+$) state by a chemical reaction (or reactions).

Authors' Abstract

Compressibility

Beattie, J. A., Brierley, J. S., and Barriault, R. J. THE COMPRESSIBILITY OF KRYPTON. I. AN EQUATION OF STATE FOR KRYPTON AND THE WEIGHT OF A LITER OF KRYPTON. *J. Chem. Physics*, **20**, 1613-1615 (1952) October.

The compressibility of krypton containing 0.90 mole percent xenon has been measured from 0° to 300° C. and over the density range 1 to 10 mole per liter. The constants for pure krypton are R = 0.08206, A_o = 2.4230, a = 0.02865, B_o = 0.05261, b = 0, c = 14.89 × 10^4 in units of standard atmos, liters per mole, and °K (T°K = t°C + 273.13). The equation for the sample studied reproduced the observed pressures with an average deviation of 0.16 percent. The weight of one liter of Kr at a pressure of one standard atmosphere is calculated from the molecular weight (83.7) and the above constants to be 3.745 g. per liter at 0°C and 3.474 g. per liter at 70° F. Authors' Abstract

Beattie, J. A., Douslin, D. R. and Levine, S. W. THE COMPRESSIBILITY OF AND AN EQUATION OF STATE FOR GASEOUS NEOPENTANE. *J. Chem. Physics*, 1619-1620 (1952) October.

The compressibility of gaseous neopentane (2-2 dimethyl propane) has been measured from 160.60°, the critical temperature, to 275° over a density range from 1 to 7 mole per liter, the maximum pressure being about 300 atmos. The constants of the Beattie-Bridgeman equation of state for the gas phase are R=0.08206, A_o = 23.3300, a = 0.15174, B_o = 0.33560, b = 0.13358, c = 400X10^4 in units of normal atmos, liter per mole, °K (T°K = t°C + 273.13), the molecular weight being taken as 72.0924 g. per mole. The second virial coefficients were determined graphically at each temperature.

Authors' Abstract

Beattie, J. A., Levine, S. W. and Douslin, D. R. THE COMPRESSIBILITY OF AND AN EQUATION OF STATE FOR GASEOUS NORMAL PENTANE. *J. Am. Chem. Soc.*, **74**, 4778-4779 (1952) October 5.

The compressibilities of normal pentane have been measured from 200 to 300° and from a density of 1 to 7 moles per liter, the maximum pressure being 350 atm. The constants of the Beattie-Bridgeman equation of state for normal pentane are R = 0.08206, A_o = 28.2600, a = 0.15099, B_o = 0.39400, b = 0.39400, b = 0.13960, c = 400 × 10^4, molecular weight = 72.0924 in units of normal atm., liter per mole, °K. (T°K. = 1, °C. + 273.13). The second virial coefficients were also determined to three significant places from 200 to 300°.

Authors' Abstract

Equilibrium Calculations

Rachford, H. H., Jr. and Rice, J. D. PROCEDURE FOR USE OF ELECTRONIC DIGITAL COMPUTORS IN CALCULATING FLASH VAPORIZATION HYDROCARBON EQUILIBRIUM. *J. Petroleum Techn.*, **4**, 19 (1952) October.

A procedure for using a digital computor to solve the equilibrium flash vaporization equation for multicompount mixtures is outlined. The method is well suited to sequence-controlled computing equipment. The method is not limited to equilibrium calculations and may be used for solution of most implicit equations in one variable. O. T. Bloomer

Heat Capacities

Schlinger, W. G. and Sage, B. H. ISOBARIC HEAT CAPACITIES AT BUBBLE POINT. *Ind. Eng. Chem.*, **44**, 2454-2470 (1952) October.

The isochoric heat capacities of cis-2-butene, isopropyl benzene, and n-decane were measured at temperatures from 70° to 220° F. The measurements were made in the heterogeneous re-

gion with two different quantities of the compounds, and the isobaric heat capacity at the bubble-point was established from these measurements using suitable thermodynamic relations. O. T. Bloomer

Infra-Red Spectra

Cannon, C. G. and Sutherland, G. B. THE INFRA-RED ABSORPTION SPECTRA OF SOME AROMATIC COMPOUNDS. *Spectrochimica Acta*, **4**, 373-395 (1952) 1951.

The infrared spectra of several aromatic compounds are presented, together with a description of the apparatus, specimens, and techniques employed in obtaining this data. An attempt is made to correlate the spectral data with molecular structure. R. Parker

Phase Behavior

Selleck, F. T., Carmichael, L. R. and Sage, B. H. PHASE BEHAVIOR IN THE HYDROGEN SULFIDE-WATER SYSTEM. *Ind. Eng. Chem.*, **44**, 2219-2226 (1952) September.

The equilibrium pressures at three-phase states associated with one of the quadruple points of the hydrogen sulphide-water system were determined at temperatures between 40° F. and 340° F. Throughout this temperature range the bubble-point pressure of the aqueous liquid phase was determined as a function of composition and temperature, at states where hydrate formation was not encountered, for pressures up to 2500 psia. The quantity of water in the gas phase was investigated in the same range of temperature and for pressures up to 5200 psia. It was found that hydrates of hydrogen sulphide exist at temperatures as high as 90° F. for pressures in the neighborhood of 7000 psi. O. T. Bloomer

Sulfur Thermodynamics

Evans, W. H. and Wagman, D. D. THERMODYNAMICS OF SOME SIMPLE SULFUR-CONTAINING MOLECULES. *J. Research Nat. Bur. Standards*, **40**, 141-148 (1952) September.

The thermodynamic functions $(F^\circ - H_o^\circ)$ T, S° $(H^\circ - H_o^\circ)$, and C_p° are calculated to high temperatures for gaseous sulfur (monatomic and diatomic), sulfur monoxide, sulfur dioxide, sulfur trioxide, and hydrogen sulfide from molecular and spectroscopic data. Values of the heats of formation of the various atomic and molecular species are selected from published experimental data, and certain industrially important equilibria are calculated. Authors' Abstract

Water Gas Shift

Ingles, O. G. THE WATER GAS SHIFT REACTION IN FUEL SYSTEMS. PART I. THE WATER GAS SHIFT ON CARBON. *Trans. Faraday Soc.*, **48**, 706-712 (1952) August.

Experimental results on the study of the water-gas shift reaction on purified sugar carbon between 750° and 850° C. indicate that initial presence of H2 increased the reaction rate, and a kinetic mechanism was postulated accordingly where H atoms assisted in the transfer of an oxygen atom to a carbon monoxide molecule. The derived equations arising from this appear to agree experimentally. S. Mori

The following articles, the abstracts for which appear on the pages indicated, are also called to your attention:

Lumpkin, H. E. HYDROCARBON TYPE ANALYSIS BY MASS SPECTROSCOPY. p. 234

Rose, H. E. THE PERMEABILITY METHOD OF SPECIFIC SURFACE DETERMINATION. p. 234

9. ORGANIC CHEMISTRY

Coal-Tar Properties

Vahrman, M. SOME ASPECTS OF THE CHEMISTRY OF COAL TARS. I. CHEMICAL NATURE. II. GENERAL CHARACTERISTICS AND CHEMICAL COMPOSITION OF DOWN-JET TARS. *J. Applied Chem.* (British), **2**, 532-538 (1952) September.

In paper I the physical and chemical properties of coal tars of differing origin are reviewed, including general observations on types of linkages, amorphous constituents, constituents fractionated by solvent extraction, and products formed by pyrolysis and by oxidation and polymerization treatments. In paper II experimental work on examination of a "down-jet" tar with respect to physical properties, distillation analysis and solvent fractionation are presented. D. M. Mason

Hydrocarbon Structure

Waterman, H. I. and Booy, H. THE CONNECTION BETWEEN THE SPECIFIC REFRACTION, THE DISPERSION AND THE STRUCTURE OF SATURATED HYDROCARBON MIXTURES. *Analytica Chimica Acta*, 7, 277-285 (1952) September.

The method of determining the number of rings in saturated hydrocarbon mixtures with sufficient accuracy from the specific refraction and the dispersion was indicated. With this method the molecular weight of the mixture need not be known. Authors' Abstract

Hydrocarbon Reforming

Haensel, V. and Sterba, M. J. PYROLYTIC AND CATALYTIC DECOMPOSITION OF HYDROCARBONS. *Ind. Eng. Chem.*, 44, 2073-2081 (1952) September.

In the field of hydrocarbon decomposition reactions, the year ending in May, 1952, has been highlighted by the appearance and description of a variety of catalytic reforming processes for the production of aromatics and high octane number gasolines from virgin naphthas. There has been a continued appearance in the literature of the results of research work which elucidates decomposition reaction mechanisms and the mode of catalyst participation in these reactions. The petroleum refining industry is giving an increasing amount of attention to the production of petrochemicals, particularly aromatics and ethylene. Catalytic cracking capacity and catalyst manufacturing facilities continue to increase. Coking processes have received greater than usual attention, during the past year, in the industrial literature on thermal cracking. Authors' Abstract

Pure Tar Acids

Savitt, S. A. and Othmer, D. F. SEPARATION OF m- AND p-CRESOLS FROM THEIR MIXTURES. *Ind. Eng. Chem.*, 44, 2428-2431 (1952) October.

Due to differences in the freezing point curves of meta and para cresols with benzidine, a method of separation involving precipitation of para-cresol with this reagent has been devised. This separation is effected in fewer steps than the original procedure of Bentley. Purities as high as 98% can be obtained as compared with 85% by the Bentley method. R. Parker

10. CHEMICAL ENGINEERING

Adsorption

Browning, F. M. ADSORPTION: VAPOR PHASE PROCESSES SERVE INDUSTRY WELL. *Chem. Eng.*, 59, 158-161 (1952) October.

Solvent recovery by means of activated carbon in fixed-bed units can be used to recover almost all commonly used industrial solvents, with overall recovery efficiencies of 80-95%. A new process, called hypersorption, employs a moving bed of activated carbon for the separation of hydrocarbons. Purification of industrial gases is accomplished at elevated pressures using thick beds of activated carbon. The usual industrial dehydration adsorbents are silica gel, activated alumina and activated bauxite in fixed-bed units. J. D. Parent

Helbig, W. A. ADSORPTION: LIQUID PHASE PROCESSES ARE IMPORTANT. *Chem. Eng.*, 59, 153-157 (1952) October.

This article discusses the selection of the proper adsorbent for liquid phase systems, as well as the considerations which enter into the choice between the powdered or granular forms, the effects of process variables on the efficiency of adsorption, adsorbent regeneration and the physical properties of adsorbents which affect the selection of equipment and materials of construction. The advantages of the Freundlich adsorption isotherm for evaluating adsorption efficiencies are stressed. J. D. Parent

Treybal, R. E. ADSORPTION TECHNIQUES ARE IDEAL FOR DIFFICULT SEPARATIONS. *Chem. Eng.*, 59, 150-152 (1952) October.

The advantages and limitations of adsorption as a separation operation are pointed out be comparison with the more familiar separation processes such as absorption and distillation. Selectivity according to the type of absorbent used and the molecular weight and chemical-type of adsorbate makes the adsorption method especially useful for making difficult separations. Adsorption processes such as contact filtration, percolation or fixed-bed adsorption and continuous fractional adsorption are described

and related to more familiar separation processes in an attempt to understand their characteristics. J. D. Parent

Heat Transfer

Carberry, J. J. Re, Pr, Nu, St, Pe: WHAT'S THEIR REAL SIGNIFICANCE? *Chem. Eng.*, 59, 144-148 (1952) September.

The author presents a review of the current literature on the application of the three basic dimensionless groups to mass and heat transfer. The material presented is a restatement of the ideas presented by Reynolds, and their further developments up to and including the work of Martinelli. The ideas and basis for "J" factors and mixing length as well as the physical concepts of the dimensionless groups are discussed. R. E. Peck

Dolezal, R. IMPROVED UTILIZATION OF WASTE HEAT. *Combustion*, 24, 57-58 (1952) September.

Thin-walled tubes of a smaller diameter were inserted into the existing tubes of a waste-heat boiler thereby increasing the heat transfer through the tubes. Under this arrangement there is the added heat transfer by radiation from the inner to the external tube. Improved efficiency and increased output resulted with no difficulty with the exhaust gas stream due to the modification. E. J. Pyrcioch

Oxygen Plants

Roberts, I. TONNAGE OXYGEN PLANTS. *Refrigerating Eng.*, 60, 950-953, 992-996 (1952) September.

Engineering factors are discussed in the design of the distillation plant operating at - 300 F., including the arrangement of the cold box, insulation, valves and seals. C. von Fredersdorff

Water Supply

THE WORLD OF WATER. *Power*, 96, ,73-118 (1952) September.

A thorough and complete survey is given of all of the current major problems in securing a permanent and satisfactory water supply. Part one explains the sources of water supply and how it is carried; part two gives pertinent information needed in planning a complete water supply for an industrial plant. W. G. Bair

11. PROCESS EQUIPMENT AND INSTRUMENTATION

Gas Meter

Mellen, G. L. (assigned to National Research Corp.) VELOCITY METERING OF GAS FLOW. U.S. 2,611,268 (1952) September 23.

The meter consists of a source of ionizing activity positioned in such a way that equal numbers of ions are collected at two sets of electrodes when the gas is not moving between them. I. P. Patel

Gas Mixing

CHICAGO'S NATURAL GAS JET "PULLS" MANUFACTURED GAS INTO SYSTEM. *Gas*, 28, 38-39 (1952) September.

The pressure of the incoming natural gas is used to "pull" the manufactured gas into the system and to deliver the mixture at the required pressure. E. F. Searight

Network Analyzer

Barker, C. L. COMPUTING FLOW CONDITIONS IN GAS LINES WITH THE McILROY ANALYZER. *Pipe Line News*, 24, 21, 22 (1952) August.

The article is a description of the McIlroy network analyzer, and a brief explanation of its operation. It also includes tables of results from a problem worked to illustrate the use of the analyzer. R. A. Brown

Haupt, L. M. PIPE LINE FLUID NETWORK CALCULATOR. *Petroleum Eng.*, 24, D33-D34 (1952) September.

The problem of determining flow distribution and head loss in large fluid systems, the fundamental relationships involved, and the linear and non-linear types of network analyzers are presented. A sample problem is set up and solved using the latter type of network calculator. R. A. Brown

Pipe Line Testing

Brinckley, M. J. USE OF PIGS IN HYDROSTATIC TESTS OF LARGE PIPE LINES. *Pipe Line News*, 24, 33-37 (1952) September.

Procedures were developed for the use of pigs in hydrostatic testing of 30-inch pipe lines from experience gained for following their use in several sections of gas pipe line during both the water filling and meter removal operations. A

profile of the top of the pipeline plotted against a pressure scale representing the static head of water is essential. Anticipated pressures which will occur during the movement of the pig should be plotted. Planning for the test should take into account such additional factors as pressures, volumes, time, water and gas supply points, and points where gas and meter may be released from the line. E. J. Pyrcioch

The following article, the abstract for which appears on the page indicated, is also called to your attention:

Rachford, H. H., Jr. ELECTRONIC COMPUTORS IN CALCULATING EQUILIBRIUM. p. 236

12. MATERIALS OF CONSTRUCTION

Cathodic Protection

Howell, R. P. POTENTIAL MEASUREMENTS IN CATHODIC PROTECTION DESIGNS. *Corrosion*, 8, 300-304 (1952) September.

Criteria for determining effective cathodic protection are listed as: 1) Current density; useful when current density required for protection is known and the design of the structure lends itself to reasonably accurate determination of current pickup. 2) Potential change; the author believes a potential change of 0.3 volt is adequate but suspects it results in over-protection. Polarization effects may obscure significance of measurements. 3) Current-potential curves; elaborate equipment is required and the method is time consuming. 4) Copper-sulfate Potential: the accepted criterion of 0.85 volt loses some of its validity in highly aerated soils. Methods, instruments, techniques and examples of potential measurements are given. Multiple-rectifier systems, pipe lines in salt water, steel structures in salt water, and oil and gas well casings are considered. Author's Abstract

Coatings

PREVENTION OF MACHINERY CORROSION. *Ind. Finishing* (British), 5, 102-113 (1952) September.

The article contains some interesting color photographs of corrosion of stainless and plain steel showing the effects of protective coatings. W. G. Bair

Corrosion Inhibitors

Lytle, M. L. (assigned to Standard Oil Development Co.) PROCESS FOR INHIBITING CORROSION IN OIL WELLS. U. S. 2,614,980; 981; 982; 983. (1952) October 21.

An inhibitor is claimed for reducing oil-well corrosion by H2S and CO_2 respectively in the first pair of patents, which is formed by reacting 1 to 5 parts fatty acids or oil (tung, cottonseed, menhaden) with 1 part of triethanolamine or triamylamine at 300° to 550° F. In the second pair of patents similar inhibitors are formed from 1 to 3 parts fatty compounds with polyethylene glycols. The products are effective at concentrations of 0.005 to 0.1% by volume. O. P. Brysch

Fire Retardants

Suggitt, J. W. EVALUATION OF FIRE RETARDANT PAINTS. *Can. Chem. Processing*, 36, 90, 91 (1952) September.

The reproducible tests developed at the Ontario Hydro Research Laboratory give a reliable estimate of fire retardant properties. In all, six types of coatings were tested for their fire-retardant ability. Other properties including washability, workability, appearance and adhesion, covering power, drying time, and flammability of the paint during application were also tested. Author's Abstract

Structural Carbons

Oliver, J. P. CARBON AND GRAPHITE. *Chem. Eng.*, 59, 276-278 (1952) September.

The corrosion resistance properties of carbon and graphite including the impervious varieties are presented, along with data on their physical properties, available forms and applications. Chemical resistance to the action of most acids, alkalis, organic compounds and other chemicals not characterized as strong oxidizing agents has led to the widespread use of carbon and graphite as construction materials in the chemical industry. The impervious forms are made by impregnating graphite, (which is not entirely impermeable to fluids) with chemical resistant, thermosetting resins. Chemical resistance properties of impervious carbon and graphite at various temperatures and concentrations of chemicals are shown in chart-form. R. J. Dennison

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INSTITUTE OF GAS TECHNOLOGY

RESEARCH BULLETIN

10

SULFUR POISONING OF NICKEL CATALYSTS

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RESEARCH BULLETIN

10

SULFUR POISONING OF NICKEL CATALYSTS

The Effects of Sulfur Composition, Sulfur Concentration and Rates of Natural Gasoline Feed Upon Conversion Efficiency and Catalyst Life of a Nickel Cracking Catalyst

and

A Brief Study of Nickel Sulfide Catalysts for the Cracking of Natural Gas

By

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PREFACE

This bulletin is the tenth in a series of publications on research conducted in the laboratories of the Institute of Gas Technology. The work described in this bulletin is a continuation of the study of "Catalysts for Gaseous Reactions," * Project CPR-7, sponsored by the Gas Production Research Committee under the PAR (Promotion-Advertising-Research) Plan of the American Gas Association. This report presents two phases of that program conducted during 1950:

1) Study of the effects of specific sulfur compounds, with and without process air additions, upon the catalytic steam-gasification of natural gasoline into blue gas equivalents when using a commercial nickel catalyst.
2) The development of a "sulfur-active" catalyst of nickel sulfide for the steam conversion of natural gas into carbon monoxide and hydrogen, such a catalyst requiring hydrogen sulfide in the reacting gases to maintain the catalyst in a sulfided state.

The first phase of the program has been financed by the Gas Production Research Committee, and the second phase by the International Nickel Company as a cooperative project with the Gas Production Research Committee.

The guidance of the Supervising Committee in planning the work is gratefully acknowledged. T. L. Robey, Coordinator of Gas Production Research, and N. K. Chaney, Research Consultant, have provided helpful contributions in orienting the investigations. The following members of the staff of the Institute of Gas Technology participated in the experimental work: H. A. Dirksen, E. Kovacic, J. McGarvey, C. Pierson, D. Werle, and I. Williams, under the supervision of Dr. C. H. Riesz.

Chicago, Illinois
September, 1951

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*Riesz, C. H., Komarewsky, V. I., Kane, L. J., Estes, F. and Lurie, P., "Catalytic Gasification of Higher Hydrocarbons," *AGA Monthly* **28**, 159-164, 190 (1946).
Batchelder, H. R., "Sulfur Resistant Catalysts," *AGA Monthly* **29**, 222-225, 232 (1947).
Riesz, C. H., "Catalytic Cracking of Hydrocarbons," *AGA Proceedings* (1948), 505-16.
Riesz, C. H., Batchelder, H. R. and Lurie, P. C., "Catalytic Reforming of Hydrocarbons," *AGA Monthly* **30**, February, 17-22 (1948).
Riesz, C. H., Lister, F. Smith, L. G. and Komarewsky, V. I., "Catalysts for Hydrocarbon Synthesis," *Ind. Eng. Chem.* **40**, 718-722 (1948).
Riesz, C. H., Lurie, P. C. and First, J. J., "Catalytic Reforming of Hydrocarbons," *AGA Monthly* **30**, April, 17-20 (1948).
Sebastian, J. J. S. and Riesz, C. H., "Sulfur-Resistant Catalysts for Reforming Propane," *Ind. Eng. Chem.* **43**, 860-866 (1951).

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ABSTRACT

By the beginning of 1950 it was apparent that catalytic cracking had achieved acceptance as an important means of producing peak load and base load water gas equivalents, especially in the Eastern area of the United States. This acceptance had been predicated upon the use of low-sulfur feed stocks to avoid the investment costs of sulfur-purifying equipment hitherto considered necessary when using highly active nickel catalysts.

The work described herein was conducted during 1950 and was directed to a determination of the effects of various kinds of organic sulfur and the amounts which industrial units might be expected to tolerate when operated for the production of fuel gas. A systematic study was made of the relative performance life and activity of a commercial nickel catalyst when steam-gasifying a natural gasoline to which various sulfur compounds were added in controlled concentrations.

The results obtained in this limited laboratory system appear to have broad significance. First, the catalyst life, or capacity before regeneration becomes necessary, and the catalyst conversion efficiency, are found to vary widely and independently with the kind as well as the amount of sulfur compound present.

Second, the performance of nickel catalysts in the presence of sulfur can be improved considerably by appropriate selection of feed rates, steam concentrations, and operating temperatures. Specifically, the addition of process air invariably lengthens the operating period before regeneration becomes necessary.

Third, no permanent impairment of the nickel catalyst need be caused by sulfur in any amount or form if proper conditions of catalyst regeneration are observed. In every case it was found possible to restore the catalyst to its original effectiveness, provided excessive temperatures during regeneration were avoided. Thus the economics of sulfur purification is directly resolvable by balancing its cost against the loss of plant capacity due to downtime for catalyst regeneration and to decreased catalyst activity.

As an alternative approach some "sulfur-active" nickel sulfide catalysts, prepared under the auspices of the International Nickel Company at Mellon Institute, were tested for use in catalytic cracking. Results obtained in the catalytic steam reforming of natural gas indicate that at the relatively lower temperature levels required, nickel sulfide catalysts are not sufficiently active to be competitive with the commercial metallic nickel catalysts now in use.

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THE PROBLEM

Industrial applications of catalysis for gas manufacture by public utilities in the United States are relatively new and thus far have been limited to reactions between hydrocarbons and steam for the production of blue gas equivalents. Commercial cracking catalysts used in these installations consist of metallic nickel suitably dispersed upon porous ceramic supports. The capacity and operating efficiency of these plants have been reduced through a loss of activity, "poisoning," of the catalysts by exposure to the amounts of sulfur present in the hydrocarbon feed stocks.

The objective of the first phase of this investigation was to determine whether the chemical composition of the sulfur compounds exerted specific effects upon the severity or nature of the catalyst poisoning, and how these effects were modified by the admixture of air with the steam.

The objective of the second phase of this investigation was to determine whether the problem of catalyst poisoning by sulfur compounds could be circumvented by the preparation of a catalytically active form of nickel sulfide, a so-called "sulfur-active" catalyst, which would be chemically immune to further changes caused by reaction with sulfur.

SUMMARY AND CONCLUSIONS

1. The Sulfur Poisoning of Nickel Cracking Catalysts.

Sulfur poisoning manifests itself in two distinct ways:

1) by accelerating the normal rates of carbon deposition on and within the catalyst granules.
2) by lessening the completeness of the hydrocarbon conversion to carbon monoxide and hydrogen.

A method of evaluating the first of these effects is based upon the fact that the accumulation of carbonaceous deposits on the catalyst granules finally becomes sufficiently great to make it impossible to maintain the initial rates of hydrocarbon feed. Catalyst bed conditions can be selected so that the pressure differential across the catalyst bed will rise steeply toward the close of the close of the test. The operating life of the catalyst, thus indicated, may be expressed in terms of the volume of product gas which can be made per cubic foot of catalyst before shutdown is required.

The second criterion of catalyst performance, the relative completeness of the hydrocarbon conversion to carbon monoxide and hydrogen, is indicated by the relative heating values of the product gases. The heating values are found to be specifically affected by the chemical composition as well as by the amount of sulfur compounds.

Table A summarizes the experimental data on a series of sulfur compounds according to these two criteria. The compounds are arranged in four groups in the order of increasing toxicity as indicated by decreased operating life in the MCF of carrier gas made per CF of catalyst before regeneration was required to remove deposited carbon. The corresponding data on efficiency of hydrocarbon conversion as measured by the Btu of the product gas appear in the second column. The numerals in the last column represent the relative order of increasing toxicity of these sulfur compounds as indicated by decreasing hydrocarbon conversion; it will be noted that there

TABLE A

Effect of Type of Sulfur Upon Conversion Efficiency and Catalyst Life

SULFUR COMPOUND	Capacity MCF/CF Catalyst	Conversion Efficiency Btu/CF	Rank of Conversion Efficiency
GROUP I			
Thiophene	38	386	5
Tertiary Butyl Mercaptan	38	362	1
GROUP II			
Tertiary Dodecyl Mercaptan	33	383	4
Ethyl Mercaptan	32	447	10
Hydrogen Sulfide	29	417	8
GROUP III			
Normal Propyl Mercaptan	23	377	2
Dimethyl Sulfide	20	410	6
Diethyl Sulfide	17	487	11
GROUP IV			
Tertiary Hexadecyl Mercaptan	12	420	9
Thiophenol	11	381	3
Carbon Disulfide	11	411	7
Sulfur Concentration Weight %		= 0.08 ± 0.002	
Oxygen Feed Rate		= Zero	
Gasoline Feed Rate Gals/CF Cat-Hr		= 1.25 ± 0.06	

is no relationship or correlation between catalyst service life as determined by rates of carbon deposition, and catalyst conversion activity as determined by the Btu of the carrier gases. The conclusion indicated by this evidence is, therefore, that the chemical composition of the sulfur exerts not only specific, but independent, effects respectively upon the rates of carbon deposition and upon the catalyst conversion efficiency.

A possible clue to this lack of correlation between carbon deposition and catalytic activity is found in the observation that sulfur may be retained by the catalyst after substantial removal of the carbon, and that the conversion activity of the catalyst is lowered by such retention, and restored by subsequent removal of the sulfur. That is to say, the acceleration of the normal rates of carbon deposition by sulfur, and the sulfiding of the active nickel by sulfur, appear to be two independent reactions, the rates of which are independently affected by the chemical composition of the sulfur.

2. The Effect of Process Air on Sulfur Poisoning.

This investigation as summarized in Table B shows that air, when admixed with the process steam, always lengthens the service life of the catalyst by reducing the rate of carbon accumulation. Again, the degree of improvement varies with the chemical composition of the sulfur, and other operating conditions. On the other hand, the effect of process air upon the conversion activity or efficiency of the catalyst as determined by the Btu of the product on a nitrogen-free basis, while usually beneficial, may be adverse as shown in the case of the tertiary butyl mercaptan tests recorded in Table B.

3. Effects of Sulfur Concentration and Rates of Hydrocarbon Feed Upon Sulfur Poisoning.

While the chemical form of the sulfur appears to affect the relative performance of the catalyst with respect to operating life and efficiency, the order of magnitude of these effects may be considerably modified by the choice of operating conditions with respect to steam ratios, feed rates, operating temperatures, and levels of sulfur concentration. Table C summarizes the data for: 1) the effect of increasing sulfur concentrations in the gasoline feed, and 2) the effect of increasing the rate of gasoline feed, upon the catalyst life and Btu of the product gas. Typical life test curves at

TABLE B — EFFECT OF PROCESS AIR UPON CONVERSION EFFICIENCY AND CATALYST LIFE

		OPERATING CONDITIONS				CONVERSION EFFICIENCY		CATALYST LIFE		
Run No.	Sulfur Compound	Sulfur Wt. % of Gasoline	Air/C Ratio	Steam/C Ratio	Gasoline Gal/CF-Hr	CF/Gal Gasoline	N.F. V Btu/CF	CF/CF Cat. Hr	Total MCF/CF Catalyst	Duration Hours
79	None	0.011	0	6.6	3.2	440	339	1390	141	94
80	None	0.012	0.88	6.1	3.4	500	332	1680	175	105
	GROUP I									
1	Thiophene	0.039	0	6.2	3.3	180	669	600	21	29
6		0.039	0.81	6.4	3.2	370	458	1180	44	36
4		0.079	0	8.2	1.3	330	417	420	44	100
9		0.079	0.34	8.3	1.3	410	363	520	55	110
17	Tertiary Butyl Mercaptan	0.082	0	9.0	2.2	290	491	610	16	43
23		0.088	0.55	8.6	2.3	280	579	650	31	43
	GROUP II									
28	Ethyl Mercaptan	0.015	0	6.4	3.7	320	407	1060	109	104
37		0.015	0.84	6.3	3.3	500	341	1610	178	108
29		0.021	0	6.3	3.8	240	438	800	32	45
38		0.022	0.80	6.3	3.8	450	363	1480	150	101
34		0.082	0	6.3	3.2	170	730	550	16	29
43		0.082	0.78	6.4	3.2	320	531	1000	51	48
	GROUP III									
56	Dimethyl Sulfide	0.058	0	8.1	1.3	310	394	400	16	35
60		0.058	0.31	7.7	1.4	390	379	530	53	102
	GROUP IV									
63	TertiaryHexadecylMercaptan	0.035	0	7.9	1.3	320	386	430	25	56
67		0.035	0.33	8.6	1.2	420	334	500	38	78
64		0.046	0	8.4	1.2	380	388	450	18	37
69		0.046	0.33	8.5	1.2	400	353	500	32	65
72	Thiophenol	0.068	0	8.2	1.3	330	390	440	16	35
73		0.068	0.34	8.4	1.2	390	374	480	49	106
74	Carbon Disulfide	0.080	0	8.1	1.3	200	411	260	11	31
75		0.080	0.27	8.7	1.2	360	396	400	38	95

TABLE C —— EFFECT OF SULFUR CONCENTRATION AND GASOLINE FEED RATE UPON CONVERSION EFFICIENCY AND CATALYST LIFE

		OPERATING CONDITIONS				CONVERSION EFFICIENCY		CATALYST LIFE		
Run No.	Sulfur Compound	Sulfur Grains/100 Cf of Gasoline	Air/C Ration	Steam/C Ration	Gasoline Gal/CF Hr	Cf Gal Gasoline	N.Free H.V Btu/Cf	Cf/Cf Cat Hr	Total MCF/CF Catalyst	Duration Hours
	GROUP I									
3	Thiophene	0.052	0	8.1	1.3	490	444	370	28	72
4		0.079	0	8.2	1.3	330	417	420	44	100
5		0.083	0	8.1	1.3	390	355	500	31	66
15	Tertiary Butyl Mercaptan	0.050	0	9.4	1.1	340	390	380	39	107
16		0.077	0	10.1	1.0	370	362	350	38	107
18		0.124	0	8.9	1.1	330	352	380	15	110
19		0.148	0	7.7	1.4	290	394	440	42	36
	GROUP II									
28	Ethyl Mercaptan	0.015	0	6.4	3.7	320	407	1060	109	104
30		0.024	0	6.3	3.7	300	436	970	80	81
34		0.082	0	6.3	3.2	170	730	550	16	29
36		0.082	0	7.4	1.4	240	495	330	34	87
37		0.015	0.84	6.3	3.3	500	341	1610	178	108
38		0.022	0.80	6.3	3.8	450	363	1480	150	101
39		0.042	0.70	6.4	3.2	380	421	1230	128	105
43		0.082	0.78	6.4	3.2	320	531	1000	51	48
48	Hydrogen Sulfide	0.031	0.53	6.4	2.1	290	528	630	44	72
49		0.040	0.50	6.2	2.2	240	659	540	35	61
50		0.058	0.54	6.2	2.2	240	796	520	26	48
51		0.080	0.55	6.5	2.1	230	751	490	19	39
	GROUP III									
56	Dimethyl Sulfide	0.058	0	8.1	1.3	310	394	400	16	35
58		0.079	0	8.4	1.2	290	443	360	20	51
	GROUP IV									
63	TertiaryHexadecylMercaptan	0.035	0	7.9	1.3	320	386	430	25	56
64		0.046	0	8.4	1.2	380	388	450	18	37
66		0.128	0	8.4	1.3	280	464	350	5.2	15
67		0.035	0.33	8.6	1.2	420	334	500	38	78
68		0.035	0.78	6.2	3.3	340	470	1170	15	13

relatively high gasoline feed rates are shown in Fig. 1 for the sulfur compound, ethyl mercaptan (Group II, Table A), in which the drop in space-time yields of carrier gas is plotted against the hours of service life for increasing concentrations of sulfur, both with and without process air. Fig. 2 contains a series of life curves, obtained under the same conditions, in which the gasification yields of carrier gas are plotted against hours of service life. Thus, Fig. 2 indicates the loss in catalyst efficiency, and Fig. 1 the loss in catalyst production capacity with time, under the conditions stated. These data indicate, as would be expected, that increases in the concentration of a given kind of sulfur under given operating conditions tend to reduce both the catalyst life and the catalyst activity. Likewise, that in general an increase in the feed rates or the space velocities will have a similar effect. There is no necessary proportionality, however, between the changes in these variables and the magnitude of the effects. The specificity of chemical composition is frequently in evidence. Thus, the present studies are designed to show the relative effects of certain variables and to indicate trends and orders of magnitude, rather than to provide pre-

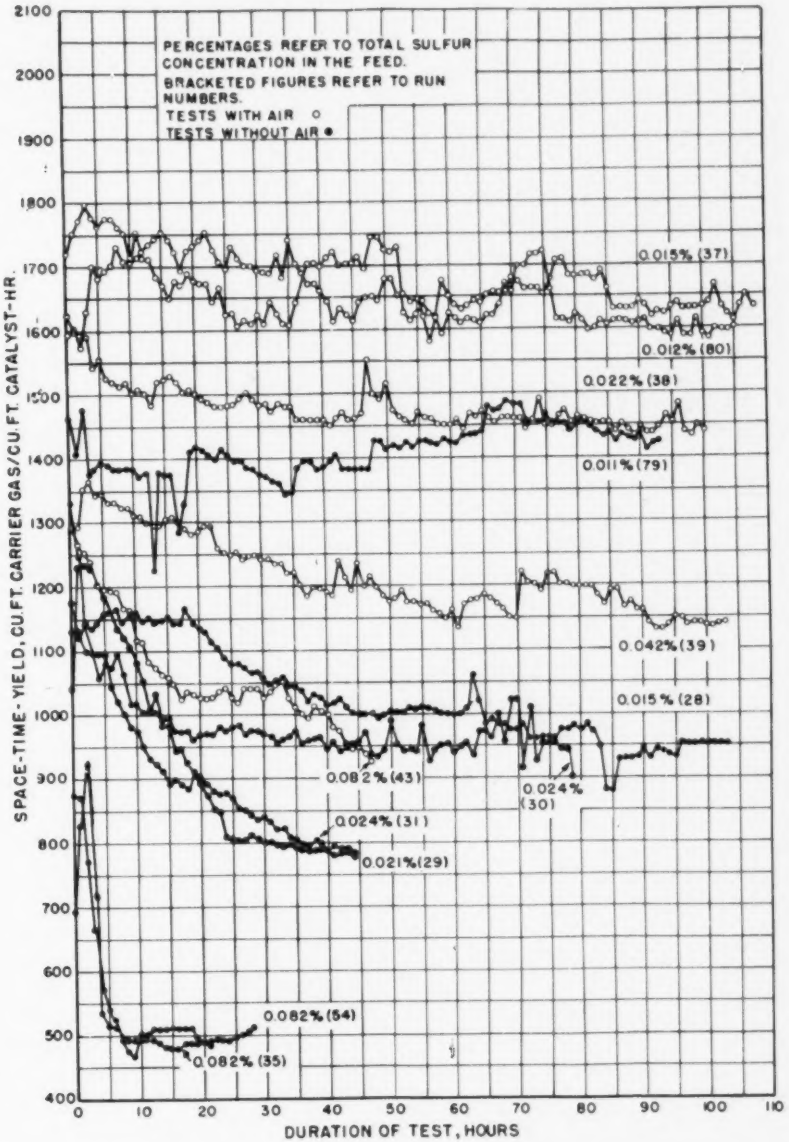


Fig. 1.—INFLUENCE OF SULFUR CONCENTRATION UPON SPACE-TIME-YIELD

cise quantitative data directly applicable to plant-scale operations.

This work has been confined to one kind of catalyst, nickel, on one kind of catalyst support, within a strictly limited range of operating variables, whereas differences in the dimensions and resistance to gas flow of the catalyst bed, the presence or absence of preheat zones, and the kind of catalyst supporting material upon which the active nickel is dispersed, may be expected to affect the over-all levels of catalyst performance. It is of interest, however, that comparisons with available plant data indicate that similar orders of magnitude for catalyst life between the regeneration periods are observed with similar sulfur concentrations. Since the chemical character of the sulfur in the gasoline itself is unknown, more precise correlations could not be expected. *

The important point of agreement between the laboratory and plant findings is that in the conversion of hydrocarbons to carbon monoxide and hydrogen by steam, no permanent impairment of a nickel catalyst need occur as a result of its prolonged exposure to high concentration of sulfur. If injury occurs it is the result of improper practices in catalyst regeneration. This simplifies the approach to the economic question of sulfur purification. Thus, provided the Btu or conversion efficiency levels obtainable with any given sulfur load meet the requirements of the user, the costs of increased sulfur purification may be balanced directly against the costs of the larger catalyst installation required to provide the necessary downtime for catalyst regeneration.

4. Regeneration of Nickel Catalysts.

This work has confirmed previous experience in the prosecution of this research project, that no permanent impairment of catalytic activity directly results from the sulfur poisoning mentioned above. It has been found possible to use the same catalyst after repeated revivification with no observable differences in its life or conversion activity. However, nickel catalysts can be seriously and permanently damaged by overheating, and are particularly subject to this kind of injury during revivification if appreciable amounts of carbon have accumulated and are burned off under conditions which allow excessive local overheating. Thus, proper control of the regeneration procedures is of the utmost importance. This is further discussed on page 14. It may be noted that regeneration must be completed with respect to sulfur as well as to carbon.

Process air may be substituted for steam to a limited extent. Optimum results were obtained using one-third of a mole of process air per mole of carbon accompanied by a reduction in the process steam from 8 moles to 6 moles per mole of carbon. Attempts to use process air in the amounts of one mole of air per mole of carbon with a reduction in process steam from 8 to 3 moles per mole of carbon resulted in reduced activity and conversion efficiency and in excessively high nitrogen contents in the carrier gases. The results obtained are included in Table I in the Appendix (page 20). These effects should be borne in mind when setting up operating conditions in plants.

5. The Preference for Nickel Catalysts in Hydrocarbon Cracking.

Favorable claims have been made by English investigators for alkali and alkaline-earth catalysts. Laboratory tests conducted in connection with this project indicate that these catalysts do not meet the operating requirements of American practice in the steam conversion of hydrocarbon gases and vapors to carbon monoxide and hydrogen. Nickel is preferred, despite its requirements for regeneration in the presence of sulfur, because it affords substantially higher space ve-

*Research Bulletin No. 3, Project PE-5, American Gas Association, New York (1951), "Peak Load Gas by Catalytic Reforming and Methanation from Commercial Sulfur-Bearing Naphtha."

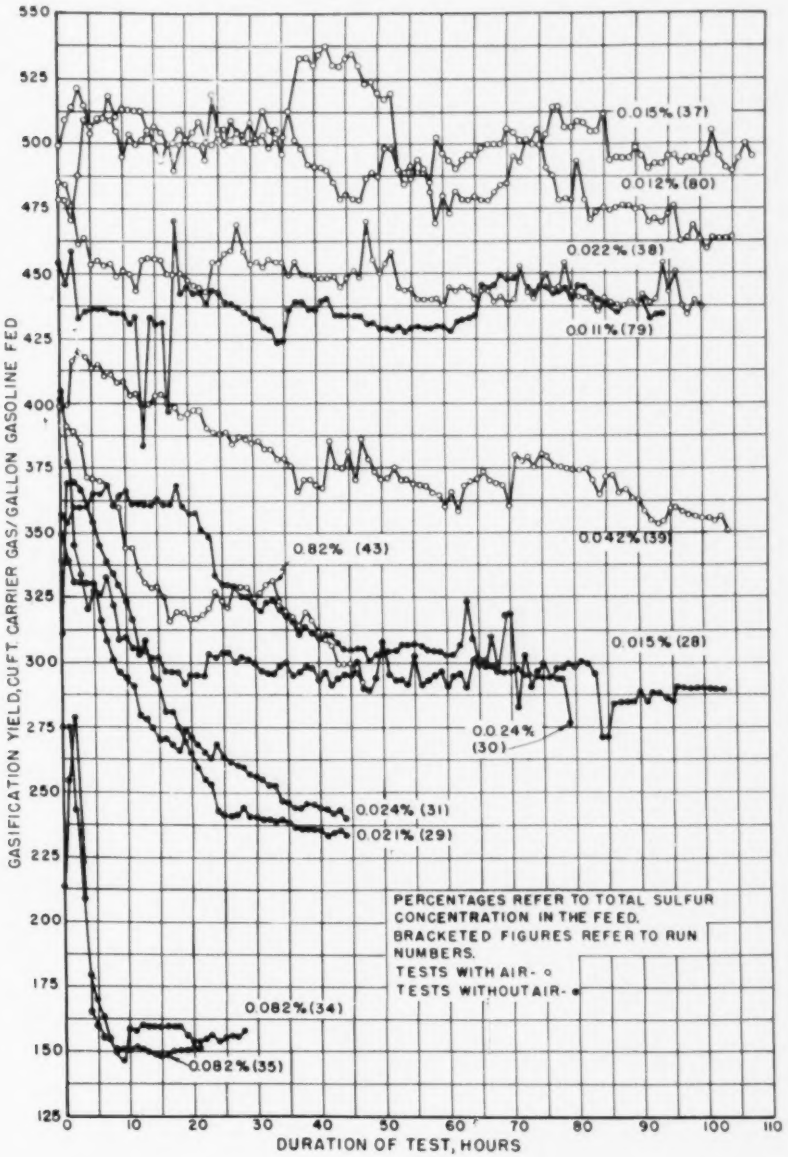


Fig. 2.—INFLUENCE OF SULFUR CONCENTRATION UPON GASIFICATION YIELD

locities with accompanying reductions in plant investment costs. The cost of nickel catalysts per MCF of gas produced has been found to be extremely small, compared to raw material and other operating costs.

6. Sulfur-Active Catalysts

A sulfur-active catalyst is characterized by the requirement that a certain concentration of sulfur in the gas phase is necessary to maintain the catalyst in the sulfide form. The catalyst evaluation study consisted of testing three alternatives in the nickel-nickel sulfide system. The first studied was a nickel-nickel sulfide solid catalyst with a melting point of approximately 1100°F; catalyst activity in this temperature range was too low for practical use. The second was a solid eutectic mixture of Ni_3S_2; catalyst activity was too low and temperature control too critical for practical use. The third was nickel sulfide impregnated on Porocel, a commercially available bauxite carrier, promoted with alumina (0.1-1.1% mole basis) to retain the molten nickel sub-sulfide possibly by means of some sort of wetting action. This catalyst exhibited reasonable activity at temperatures of 1450 to 1490°F, the nickel sub-sulfide melting range. Some tests made at 1700°F required approximately 1,000 gr. of H_2S per CCF in the natural gas charged to insure necessary stability of the sulfide catalyst. A sharp loss in activity occurred when the hydrogen sulfide concentration was decreased below this limit.

Under favorable circumstances, the performance of the nickel sub-sulfide catalyst was considerably lower than that of a sulfur-sensitive catalyst operating at high (1750-1850°F) temperatures. The attack of the sulfur utilized to stabilize the catalyst resulted in perforation of the alloy metal tubes after brief periods of operation. Attempts to substitute ceramic coated tubes were unsuccessful; a satisfactory solution of the reactor tube corrosion problem remains to be found. Possible industrial application of the sub-sulfide catalyst appears to be limited to specific situations where large quantities of sulfur are normally associated with the hydrocarbon feed and where the presence of substantial quantities of sulfur may be tolerated in the finished gas.

DISCUSSION OF RESULTS

General Aspects of Catalyst Poisoning by Sulfur

Sulfur contamination of feedstocks has always been a major problem in catalytic processes employing nickel. These processes have become of interest to the gas industry because of recent commercial installations in the Eastern states for making carrier gas (blue gas equivalents) from hydrocarbons and steam. Substantial encouragement was given to these developments by laboratory studies showing that sulfur in the amounts presently occcurring in the available feedstocks, such as natural gas, propane, butane and refined gasolines, would not require installation of additional purification equipment.

Variations in the sulfur content of the above raw materials are appreciable. This work shows that the kind as well as the amounts of sulfur will affect both the frequency of catalyst regeneration and the completeness of hydrocarbon conversion and thus will influence 1) the suitability of the end products for any given process requirements, and 2) the amounts of catalyst which will be required to meet specified load demands. The immediate economics of hydrocarbon cracking has shown the desirability of developing more quantitative methods for determining the effects of the kind and amounts of sulfur upon plant capacities, and the extent to which these effects can be modified by admixing air with process steam.

The presence of sulfur will always impose an economic burden upon the cracking process, and a further increase above present levels will require either prior removal by purification, or an increase in the amounts of catalyst provided, to accommodate increased down-time for catalyst regeneration. The trend in natural gas, natural gasolines and refinery products is toward an increase in quantities and changes in types of sulfur present. This trend has been at a rather modest rate in the post-World War II period. However, the utility operator contemplating the purchase of new equipment needs assurance that the possible advent of higher sulfur in the feedstocks available will not impair the operability or the economics of his process.

A. Sulfur-Sensitive Nickel Catalysts

a. Range of Operating Variables. Not only may the extent of catalyst poisoning be specific to the chemical composition of the sulfur compounds, but the magnitude of the effect is sensitive to many variables, including differences in catalyst preparation and support, and operating variables such as space velocity, steam ratios and temperature. Therefore, to keep the work within bounds and make reasonable progress it was necessary to confine the tests to a limited number of variables.

Thus but one catalyst was employed — a commercial catalyst of proven ruggedness, comprising a base of Norton alundum spheres impregnated with 5% of nickel. But one reaction was studied — the formation of carbon oxides and hydrogen by reacting a hydrocarbon vapor with steam. The bulk of the tests were made with a mole ratio of steam-to-carbon of 6-to1, with a few exploratory runs at 3-to-1. The principal modification of this reaction consisted in admixing air with the steam. A temperature of 1700-1750° F was maintained. Finally, the only feedstock employed was a natural gasoline, chosen to accelerate the test program as explained below.

b. Development of Test Methods. Two criteria of catalyst poisoning were employed. The first was based upon the service life (in hours) of the catalyst before regeneration became necessary to remove the carbon deposits from the catalyst bed. This service life was then expressed in terms of the total volume of product gas made per CF of catalyst before regeneration. The endpoint of the service test was reached when the catalyst bed was blocked with carbon.

The choice of natural gasoline as the feedstock was made to accelerate this endpoint as much as possible by employing a hydrocarbon of high molecular weight having a normally high rate of carbon deposition. Any substantial acceleration of the normal rate of carbon deposition, as by appreciable sulfur poisoning, would block up the catalyst bed in less than 100 hours under the test conditions employed. On the other hand, the control tests without sulfur, and tests using certain low sulfur additions, which did not cause the catalyst bed to become blocked with carbon within 100 hours, were discontinued after this period of time. As will be noted in Table I, the "life" tests fall into two groups: one of less than 100 hours, in which the results are quantitatively comparable, and one in excess of 100 hours. The tests in the second group were discontinued on the assumption that an indicated downtime of less than 4 hours for catalyst regeneration in 100 hours of operation would be acceptable.

The second criterion was based upon the completeness of the hydrocarbon conversion to carbon monoxide and hydrogen. This was reflected in the composition of the product gas, and most conveniently by its heating value in Btu per CF. It had been noted that the completeness of hydrocarbon conversion may decrease in the first twenty-four hours, as indicated by a rise in Btu, but then usually levels off. For comparative purposes the Btu values determined in the second twenty-four hours of test have been selected as being the most comparable and significant **(Table I)**. These values will not differ substantially from the mean Btu for the entire test period, except in the case of short "life" tests, where the loss of conversion efficiency in the first twenty-four hours was high. Further, to make allowance for the nitrogen introduced with process air, the heating values were computed to a nitrogen-free basis for direct comparison of all data **(Table I)**.

c. Effects of Sulfur Composition, Sulfur Concentration and Rates of Hydrocarbon Feed. In Section 1 of the Summary and Conclusions the independence of the specific effects of sulfur composition upon catalyst life and catalyst activity respectively have been adequately discussed in connection with Table A. Likewise, in Section 3 the variables of increasing sulfur in the gasoline feedstock, and increasing rates of gasoline feed, have been indicated in connection with Table I and Table C. In Figs. 1 and 2, ethyl mercaptan was selected as a typical sulfur compound of intermediate toxicity **(Group II, Table A)**, to illustrate the effect of increasing sulfur concentrations upon space-time yields of carrier gas, and gasification yields per gallon of gasoline feed stock. A relatively high gasoline feed rate of 3.2 gallons per CF of catalyst per hour sharply magnifies the effect of the higher sulfur concentrations, as compared with the standard feed rates of about 1.1 to 1.3 gallons employed in the regular life tests. The pronounced effect of the higher feed rates in shortening the catalyst life at the higher sulfur concentrations is noteworthy.

d. The Effect of Process Air on Sulfur Poisoning. The influence of process air upon sulfur poisoning has been the subject of much experiment with results that frequently have been either inconclusive or contradictory. The present work throws some light on these discrepancies. Thus, where catalyst failure has resulted from rapid fouling of the catalyst bed by carbon, air will consistently and without exception prove helpful by increasing the length of the operating period before regeneration becomes necessary. The use of air has a beneficial effect upon the conversion efficiency; the magnitude is dependent upon the rates of feed and the chemical nature of the sulfur. (Note Table B).

It is concluded that the major effect of process air is to reduce the rate of carbon deposition and

thus prolong the operating life of the catalyst before regeneration. The process air may be substituted for steam to a limited extent. The optimum results were obtained using one-third of a mole of process air per mole of carbon accompanied by a reduction in the process steam from 8 moles to 6 moles per mole of carbon. Attempts to use process air in the amounts of one mole of air per mole of carbon with a reduction in process steam from 8 to 3 moles per mole of carbon resulted in reduced activity and conversion efficiency and in excessively high nitrogen contents in the carrier gases. The test results are presented in Table I.

e. Regeneration of Nickel Catalysts. One of the most encouraging features of this work has been the confirmation of earlier observations to the effect that sulfur poisoning, no matter how extensive, does not cause permanent injury to the active nickel. Damage can result from secondary causes, the most dangerous of which is overheating. This may easily occur through improper methods of catalyst regeneration. High local temperatures result from uncontrolled combustion of deposited carbon. Hence, the regeneration procedures are extremely important.

The preferred procedure is first to steam the catalyst bed to remove combustible gas and eliminate any tar accumulations, and to reduce the temperature below 1600°F. The second step is a controlled oxidation of the carbon by a mixture of steam and air, keeping the initial air rate low — in the order of 10 CF per hour per CF of catalyst. As the carbon dioxide content of the off gas decreases, the air rate is gradually increased to 300-400 CF per hour. This controlled oxidation is continued until the carbon dioxide concentration falls to a very low value. This step may require from three to four hours, during which time the temperature should not exceed 1800-1900°F. The last step is to discontinue the steam, and with air alone make a final cleanup of the sulfur and any traces of carbon until oxides of sulfur and carbon no longer appear in the off gases. When a regeneration procedure of this kind is employed, the use of sulfur feedstocks is limited by only two considerations. The first is the increased catalyst volume required to permit necessary down-time for regeneration. The second is the ability to maintain the desired Btu levels in the product gas.

B. Development of Sulfur-Active Nickel Catalysts

a. Nickel Sub-sulfide Catalysts. Nickel sulfide catalysts* have been termed "sulfur-active" from their need for sulfur to maintain their chemical stability and catalytic activity. Depending upon temperatures and partial pressures prevailing, an equilibrium between the sulfur-containing reactant and the nickel sulfide is established. In the present work, the steam-methane reaction was studied and hydrogen sulfide was used as a means of introducing controlled amounts of sulfur into the system. The results obtained are summarized in Table II, page 22.

b. Exploratory Tests of Sulfur-Active Nickel Catalysts. Several alternatives existed which had to be explored. First, it was important to ascertain the activity of the catalyst at temperatures of approximately 1100°F, where the nickel-nickel sulfide system was essentially in the solid state. It was found that catalyst activity in this temperature range was too low for practical operating purposes.

A second alternative was to prepare a catalyst for use under the conditions conducive to the existence of the Ni_3S_2 eutectic mixture. A small but definite degree of cracking activity was found. However, the control of temperature and other variables proved too critical to justify further study of this procedure.

A third alternative, to provide in the feed gas an excess of hydrogen sulfide over that necessary to maintain nickel sub-sulfide, was adopted for the balance of the test program. The nickel was impregnated on a carrier capable of retaining

*Kirkpatrick, W. J., "Nickel Sulfide Catalysts" in **Advances in Catalysis**, Volume III, Academic Press, Inc. (New York) 1951, pp. 329-339.

molten nickel sub-sulfide by means of some wetting action, to insure that there was no loss of the sulfide.

c. Selection of Catalyst Carrier. Several materials were evaluated as carriers. Porocel, a commercially available bauxite, was found to be satisfactory for the purpose. Zirconium silicate, available commercially as dense balls, was found unsuited; a porous preparation, specially prepared, was equivalent to but not better than Porocel as a carrier.

Nickel aluminate also showed promise as a carrier for nickel sub-sulfide. An attempt to sulfide a metallic nickel catalyst on an aluminum silicate base failed to produce an active catalyst.

d. Development of Nickel Sub-sulfide Catalysts. Although Porocel was found suitable as a carrier for nickel sub-sulfide, a catalyst containing only nickel sub-sulfide (about 6% mole basis) was found to be low in activity. A small amount of alumina appreciably increased the catalytic activity, possibly by supplying a satisfactory area for wetting. The improvement in conversion obtainable with concentrations varying from 0.1 to 1.1% (mole basis) is shown in Figure 3. Without alumina, the conversion was displaced to relatively low values which, moreover, were not stable, decreasing appreciably during use.

Catalysts containing 3 and 10% nickel sub-sulfide supported on Porocel and containing 0.5% alumina provided substantially the same results.

In present plant-scale catalytic cracking of natural gas with a sulfur-sensitive nickel catalyst, the activity obtained under essentially sulfur-free conditions is much greater than was found with nickel sub-sulfide catalyst. One reason for this is the considerably higher temperatures used in commercial units. Some tests were made at 1700 F with nickel sub-sulfide and indicated improvement, but nowhere near the conversion rates needed to compete with present commercial practice. The sulfur concentrations were deliberately set at high levels to insure the necessary stability of the sulfide catalyst. A sharp loss in activity occurred when the hydrogen sulfide concentration of the natural gas stream was deccreased below approximately 1000 grains per CCF.

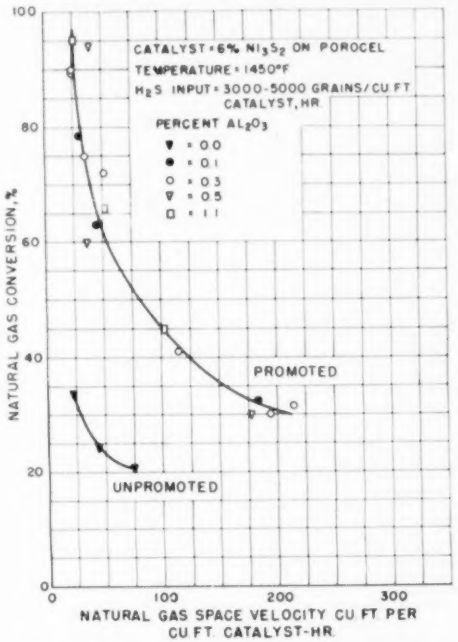


Fig. 3—Influence of an Alumina Promoter in Nickel Sub-Sulfide Catalysts

e. Corrosion of Alloy Tubes by Sulfur. During the course of the work, severe attack upon the alloy reactor tube was observed, molten sulfide coming in part from the tube exposed above the bed. Attempts to enamel the interior of the reactor tube were unsuccessful, possibly because of pin holes or small cracks which caused a concentrated attack at these points, leading to perforation. A satisfactory solution of the reactor tube corrosion problem remains to be found.

APPENDIX

A. Sulfur-Sensitive Catalyst Tests

a. Description of Catalyst Testing Units. Two of the experimental units employed in the sulfur poisoning tests were designated as Units B and C. These were essentially identical in design; the few details in which they differed will be mentioned later in the description. A simplified flow diagram which applies to both units is shown in Figure 4. Water from the tank on scale **A** was pumped by means of a Hills-McCanna duplex piston pump **B** and was converted into steam in gas-fired furnace **C**. Hydrocarbon liquid from a second tank on a separate scale was pumped by pump **B** to an alloy cross **G**. Air reduced to 18-19 psig was measured in high pressure, wet-test meter **F**, and was passed to cross **G**, where it met the steam and hydrocarbon streams. The mixture of air, steam and hydrocarbon was preheated in coil **D** maintained in electric furnace **E**, on top of the main reactor furnace **J**. The preheat coil consisted of about 23 feet of $\frac{3}{8}$-inch alloy tubing (Type 310, 25 Cr-20 Ni, Schedule 40 wall) formed into a 12-inch diameter coil.

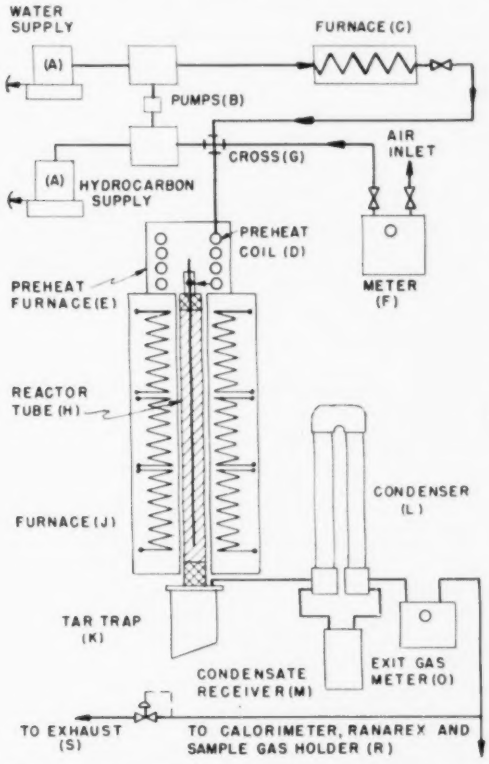


Fig. 4.—Flow Diagram of Units "B" and "C" used in Sulfur Poisoning Tests

The preheated mixture then passed through the catalyst bed contained in tube **H**, a 6-foot length of 2-inch alloy tubing (Type 310, 25 Cr-20 Ni, Schedule 40 wall in Unit B; Calite B-28 cast tube, Cr-26, Ni-11, Mn-0.8, N-0.1, Mo-1.0; 3-inch O.D., $\frac{3}{8}$-inch wall in Unit C). A catalyst bed of 48-inch depth was supported by a stainless steel screen. A thermowell of $\frac{1}{4}$-inch alloy tubing (Type 310, Schedule 40 wall) extended through the catalyst bed; three thermocouples in this well measured catalyst bed temperatures at three points. The catalyst volume was set at 0.080 CF.

The catalyst tube was surrounded for 48 inches of its length by electrical heaters arranged in a 5-inch square cross-section. Three separate zones of heating were controlled by a single controller in Unit B, and by three separate controllers in Unit C. Thermocouples peened to the catalyst tube at the center of each of the three heating zones were used to obtain the wall temperature and to control furnace operation.

A tar trap **K** was used to collect tars, if present; in the sulfur poisoning tests, negligible quantities were recovered in the trap. Cooling of the product gases and condensation of the unreacted steam was accomplished in fin-tube condenser **L**. The condensate was collected in the condensate receiver **M**. The carrier gas produced was measured by means of tin case meter **O**. Gas samples were taken continuously at **R** for analysis and for heating value and specific gravity determina-

tions. The major portion of the gas was reduced from 8 inches of water column to atmospheric pressure for venting at S.

Unit C was also provided with a pressure regulating valve (not shown) for operation of the reactor at pressures up to 100 psig. It also had a 13,000 volt precipitator (not shown) for elimination of tar fog; no tar was found by this means in any of the tests.

b. Experimental Procedure. The experimental procedure consisted of operating Units B and C with natural gasoline as feed. In most of the tests, controlled amounts of a given sulfur compound were dissolved in the feedstock to produce poisoning. A number of tests were also made with unsulfured gasoline to obtain yield data under this condition, to test the activity of the catalyst and to establish a base for comparison.

In all cases, attempts were made to secure as long a period of continuous operation as was possible in a 5-day work week and to operate under constant process conditions as specified. The pressure in these poisoning tests remained at a low value, 3 to 6 psig, for most of the operating period. At some time characteristic of the poisoning conditions, the pressure began to rise relatively rapidly, so that in 2 to 6 hours the pressure would reach 20 psig. The test was terminated at this point, to the nearest hour. In a number of tests, the pressure rose slowly if at all; such tests were stopped at the end of the week after accumulating 100 hours or more of continuous operation at constant process conditions.

c. Regeneration of Catalyst. The regeneration procedure consisted of three steps:

1) steam purge
2) air-steam regeneration
3) air regeneration

Although it may be possible to omit any of these three steps, it is believed essential that each be done in the order named for reasons of safety and effectiveness.

An initial steam purge is necessary to free the system of combustible gas and to eliminate hydrocarbon liquid accumulations and tars. The time and rates necessary will be determined mainly by experience. In the experimental work, the steaming continued for no less than 30 minutes, and was usually about 1 hour in length. The rate corresponded to that used in the tests, e.g. 50 to 100 pounds of steam per CF catalyst-hour. It is advisable to reduce the catalyst temperature to approximately 1400-1600°F prior to and during this operation.

The air-steam regeneration was the next step, and was done with increasing partial pressures of air. This is essential to insure that neither catalyst nor tube is damaged by overheating. The initial air rate can be as low as approximately 10 CF per CF catalyst-hours, increasing to a final value in the range of 300-400 CF of air per CF catalyst-hour. Additional information, such as the carbon dioxide content of the regeneration gases and catalyst temperature, can be used to check the regeneration operation. During this stage, the catalyst temperature should not exceed 1800-1900°F for nickel catalysts. The duration of the air-steam regeneration in the experimental tests was usually 3 to 4 hours.

The third step, in which air alone is used, is necessary to make a final cleanup of the sulfur, and possibly carbon, which may not have been removed in the second step. In the laboratory unit, the steam was abruptly turned off because of the difficulty in control at low steam-flow rates. In industrial operation, it is possible that a slow decrease would be made until safe air rates would be established. The air rate should be increased slowly through about the same range specified above, from 10 to a maximum of 300-400 CF per cubic foot catalyst-hour. This operation should be continued as long as any sulfur oxides or carbon dioxide remain in the regeneration gases; this took 30 minutes to 2 hours in the experimental tests.

In all cases, it was found that the initial catalyst activity was restored regardless of the degree of poisoning. The cycle was repeated successfully many times, 25 or more regenerations being possible with a single charge. When it was necessary to discharge a catalyst charge, it was always because of a thermowell or thermocouple failure.

d. Description of Alundum Sphere Catalyst. The catalyst used in all of the tests was prepared by dispersing nickel on $^3/_8$-inch alundum spheres (porosity, 38%; 70 lbs CF). The preparation consisted of impregnating the spheres with a nickel salt, followed by drying and calcining. The finished catalyst contained 4.8% by weight of metallic nickel. The alundum spheres were a product development of the Norton Company, Worcester, Mass.; the impregnation was done by the Harshaw Chemical Company, Cleveland, Ohio.

e. Natural Gasoline. The natural gasoline employed in these tests had a Reid vapor pressure of 12-13 psig and contained only a small amount of sulfur, 0.011-0.012%. The specific gravity was 0.681; the boiling range was 86-316°F in a typical sample of the feed.

f. Sulfur Compounds. Sulfur compounds, obtained from several suppliers, had boiling ranges as listed below:

BOILING RANGES OF SULFUR COMPOUNDS TESTED

SULFUR COMPOUND	Formula	Boiling Range, °F	Vendor
Tertiary Butyl Mercaptan	t-C_4H_9SH	142-170	Phillips Petroleum Co.
Tertiary Dodecyl Mercaptan	t-$C_{12}H_{25}SH$	172-207 at 5 mm	" " "
Tertiary Hexadecyl Mercaptan	t-$C_{16}H_{33}SH$	258-301 at 5 mm	" " "
Di-tertiary Butyl Disulfide	(t-$C_4H_9S)_2$	383-425	" " "
Diethyl Sulfide	$(C_2H_5)_2S$	194-197.6	Eastman Kodak Co.
Dimethyl Sulfide	$(CH_3)_2S$	100.4-102.2	" " "
Ethyl Mercaptan	C_2H_5SH	93.6-95.4	" " "
Normal Propyl Mercaptan	n-C_3H_7SH	152.6-154.4	" " "
Thiophenol	C_6H_5SH	143.6-145.4 at 15 mm	" " "
Carbon Disulfide	CS_2	114.8-116.6	Merck
Hydrogen Sulfide	H_2S	— —	Matheson, as 10% H_2S—90% N_2 mixture

Fig. 5.—CATALYST TESTING UNIT "C"

Fig. 6.—CATALYST TESTING UNIT "B"

B. Sulfur-Active Catalyst Tests

a. Description of Catalyst Testing Unit. The experimental unit used in the sulfur-active tests was designated as Unit A. The simplified flow diagram shown in Figure 7 indicates the flexibility of the unit in utilizing either gaseous or liquid feed. Since only natural gas was cracked, the use of gaseous feed will be described. Water was measured at S in calibrated burets and was pumped by means of a gear pump **Q** through rotameter **F** into an alloy coil contained in furnace **A**. The saturated steam issuing from the coil in furnace **A** was superheated in furnaces **B** and **C**. At the top of furnace **D**, the superheated steam was mixed with natural gas and hydrogen sulfide. The natural gas metered by means of a high pressure wet test meter at 10 psig entered at **L**, and then passed through rotameter **G** into the system at the top of furnace **D**. The hydrogen sulfide from a cylinder at **O** was metered in rotameter **J**, and also went into the reactant stream at the top of furnace **D**. Furnace **D** heated the reactor tube containing the catalyst. The reactor system contained in furnace **B**, **C** and **D** was comprised of $1\frac{1}{2}$-inch i.p.s. tubing, Schedule 80 wall, Type 310 alloy (25 Cr-20Ni). The catalyst bed was usually 600 cc. in volume (0.0212 CF). A thermowell of $\frac{1}{4}$-inch alloy tubing (Type 310, Schedule 40 wall) contained three thermocouples to measure catalyst bed temperature at three points in the bed.

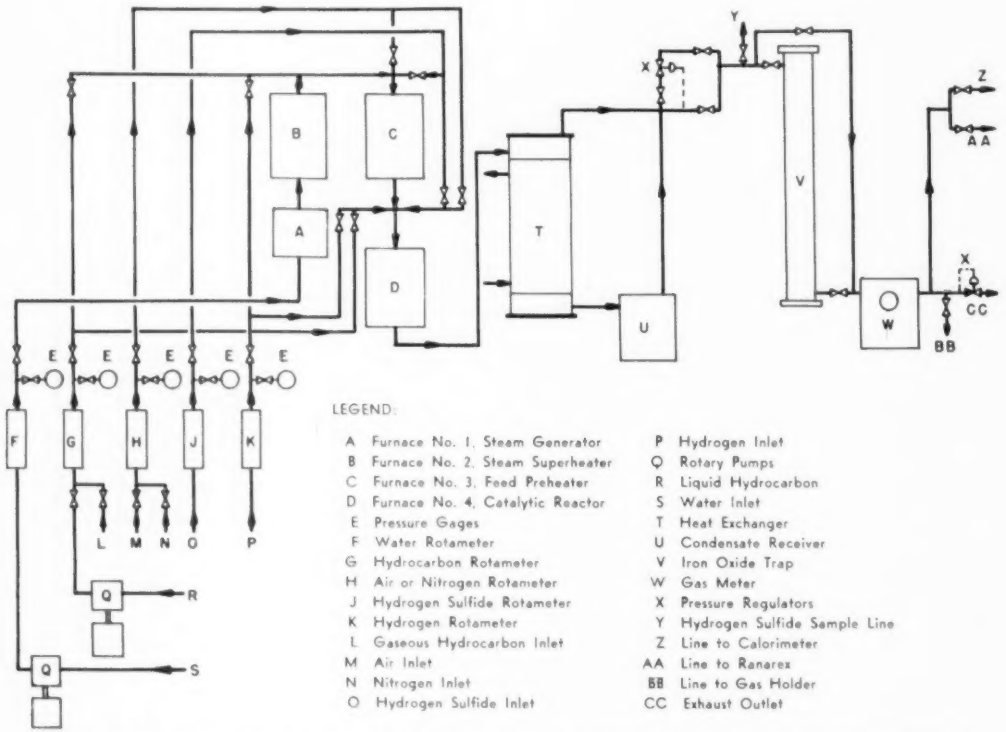
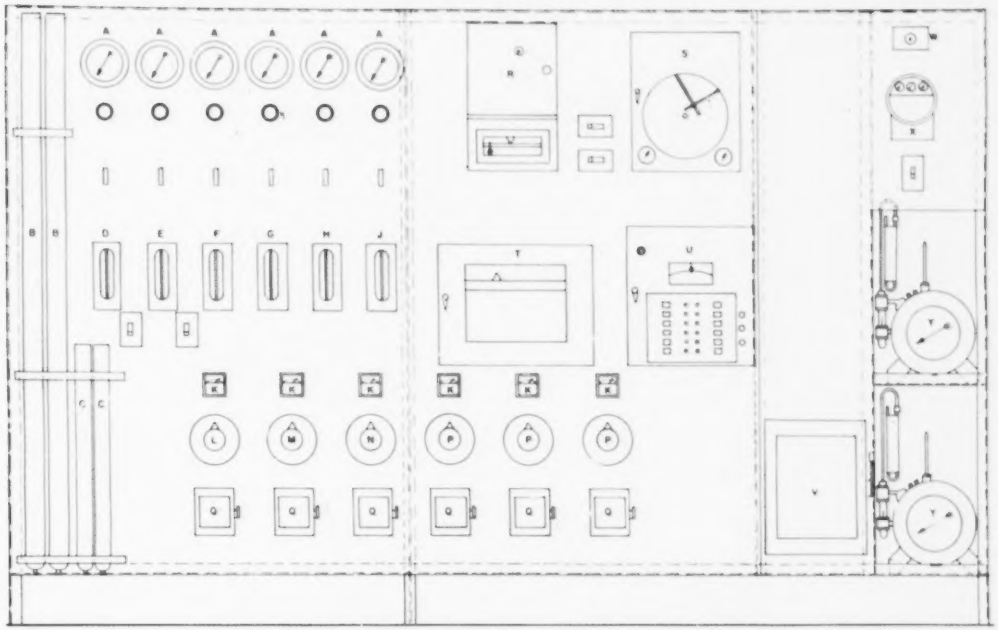


Fig. 7.—FLOW DIAGRAM OF UNIT "A" USED IN SULFUR-ACTIVE CATALYST TESTS



LEGEND:
A PRESSURE GAGES
B WATER BURETS
C HYDROCARBON BURETS
D HYDROCARBON ROTAMETER
E WATER ROTAMETER
F AIR OR NITROGEN ROTAMETER
G HYDROGEN SULFIDE ROTAMETER
H HYDROGEN ROTAMETER
J NATURAL GAS ROTAMETER
K AMMETERS
L STEAM GENERATOR VARIAC
M STEAM SUPERHEATER VARIAC
N PREHEAT FURNACE VARIAC
P VARIACS
Q 110V SWITCHES
R CAPACITROL
S PRESSURE CONTROLLER
T 12 PT. RECORDER
U 12 PT. INDICATOR
V MASTER SWITCH
W PILOT LIGHT
X WATT HOUR METER
Y EXIT METERS

Fig. 8.—INSTRUMENTATION AND DESIGN OF THE PANEL BOARD OF UNIT "A"

The gases issuing from the bottom of the reactor tube were cooled by means of exchanger **T**, the condensate being collected in receiver **U**. A high-pressure regulator **X** for pressure operation was bypassed in the present tests; the usual pressure was about 1-inch of mercury column. A sample of the gas stream was taken at **Y** for hydrogen sulfide analysis. The gas, containing relatively large quantities of hydrogen sulfide, was purified by passage through iron oxide trap **V**. A wet-test meter **W** measured the flow of purified gas. A back-pressure regulator at **X** released the bulk of the gas to exhaust **CC**. Valves at **Z**, **AA** and **BB** permitted sampling of the gas stream for heating value, specific gravity and for gas analysis.

The furnace temperatures were all hand-controlled by means of variable transformers. Temperatures were measured with an indicating potentiometer and a recording potentiometer.

The four furnaces were of the split type for ready access to the reactor tubes. The instrumentation was contained in a panel board as shown in Figure 8.

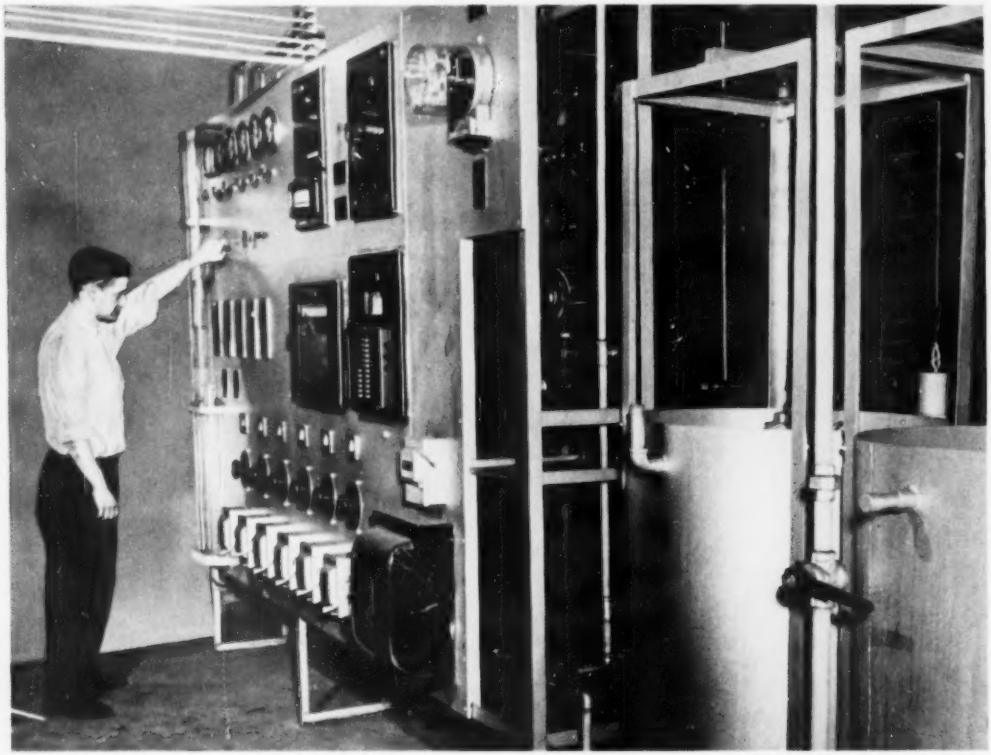


Fig. 9.—UNIT "A" EMPLOYED IN THE TESTING OF SULFUR-ACTIVE CATALYSTS

b. Experimental Procedure. The catalyst, usually 600 cc. in volume, was charged into the reactor tube in an unreduced, unsulfided form. The procedure of reducing, sulfiding and pretreating was generally as follows:

The catalyst was first reduced by passage of a stream of hydrogen at the rate of 2 CF per hour while the bed was warmed to approximately 800° F. The flow was continued for three hours or until evolution of water ceased. The temperature was then lowered to approximately 300° F. Hydrogen sulfide was then substituted for a part of this hydrogen until the hydrogen sulfide was approximately 50% of the gas stream by volume, the total flow being maintained at approximately 2 CF per hour.

When hydrogen sulfide appeared in the exit gas, as determined by analysis, the sulfiding was considered complete. The catalyst was then matured at 600° F for about three hours in a stream of hydrogen to eliminate adsorbed elemental sulfur, if present. Following this, the catalyst was rapidly heated to reaction temperature in a stream composed of equal parts by volume of hydrogen sulfide and hydrogen.

The actual test was made by first introducing steam at the desired rate, then adjusting the hydrogen sulfide rate, shutting off the hydrogen and starting the natural gas. The tests continued for from 4 to 20 hours after a hydrogen sulfide

balance had been established.

The shutting down procedure was done in the inverse order of operations described above. Normally, the temperature was dropped to approximately 1000°F overnight with approximately 2 CF per hour of a 50:50 mixture of hydrogen-hydrogen sulfide passing over the catalyst. Over week end periods, the catalyst furnace was shut down completely. Before each test, the catalyst was pretreated in accordance with the procedure used for fresh catalyst.

Occasionally carbon deposition occurred, evidenced by a low carbon balance or by a blocking of the catalyst bed. In this case, as well as before complete shutdown, the catalysts were steamed at 1100°F. The steam rate was approximately 0.1 pound per hour for this operation.

At the end of the test series for each catalyst, the catalyst was cooled in carbon dioxide to room temperature. It was discharged into a container and immediately covered with paraffin oil to prevent access of air. The samples were examined by various physical and chemical tests to determine changes in the catalyst structure.

c. Catalyst Preparation.* The catalysts were all prepared from pure nickel salts. Except for the initial exploratory catalysts, all were prepared by impregnation of the carrier with hot concentrated solutions of nickel nitrate. The mass after impregnation was heated on a steam bath with occasional stirring, and then in an oven at 230°F until dry. The catalyst was then calcined at 750°F until nitric fumes ceased to evolve.

*The sulfur-active catalysts were all prepared at Mellon Institute by W. J. Kirkpatrick, Senior Research Fellow, International Nickel Company.

Catalyst carriers used included Porocel, zirconium silicate and nickel aluminate. The Porocel was obtained from the Porocel Corporation, Philadelphia, Pennsylvania, and was designated as "Low Iron Porocel, 6/14 mesh, 2% V.M., SB-2254-50." The zirconium silicate was a natural ore pelletted into ½-inch spheres by the Orefaction Company, Pittsburgh, Pennsylvania. The nickel aluminate was prepared in the laboratory.

d. Natural Gas. The natural gas was obtained from the lines of The Peoples Gas Light and Coke Company, Crawford Station, Chicago, Illinois. The following analysis was furnished by the company:

Carbon dioxide	0.1%
Paraffins	90.4
Nitrogen	9.5
	100.0%

The following Podbielniak analysis was also furnished:

Methane	79.6%
Ethane	5.8
Propane	3.7
Isobutane	0.3
Normal butane	0.9
Pentanes	0.1
	90.4%
Paraffin index	1.19

Analysis by the Institute of Gas Technology absorption-combustion methods gave the following results:

Carbon dioxide	0.2
Illuminants	0.0
Oxygen	0.0
Hydrogen	0.0
Carbon monoxide	0.0
Paraffins	90.2
Nitrogen	9.6
	100.0
Paraffin index	1.2
Specific gravity (air = 1.00)	0.69 (calc.)
Heating value, Btu/cu.ft.	1030 (calc.)

e. Hydrogen Sulfide. Hydrogen sulfide was obtained from the Matheson Company, Inc., Joliet, Illinois. Purity is stated as 99.9% .

TABLE I—SUMMARY OF TESTS OF A NICKEL CRACKING CATALYST

		SULFUR					OPERATING CONDITIONS			CONVERSION EFFICIENCY				CATALYST LIFE		
Run No.	SULFUR COMPOUND	Wt. % of Gasoline	Grains/CF Catalyst-Hr.	Grains/CCF Reformed Gas	Pounds/CF Catalyst	Moles per Mole of Ni in Catalyst	Air/C Ratio	Steam/C Ratio	Gasoline Gal/CF-Hr.	CF/Gal Gasoline	H V Btu/CF	Sp. Gr. Air = 1.0	N-Free H V Btu/CF	CF/CF Cat.-Hr.	Total MCF/CF Catalyst	Duration Hours
79	None	0.011	14	1.0	0.19	0.11	0	6.6	3.2	440	337	0.41	339	1390	141	94
80	None	0.012	16	0.96	0.20	0.14	0.88	6.1	3.4	500	253	0.57	332	1680	175	105
						GROUP I										
1	Thiophene	0.039	52	7.3	0.22	0.13	0	6.2	3.3	180	667	0.57	669	600	21	29
2		0.046	47	6.5	0.51	0.30	0	7.9	2.6	300	460	0.47	466	750	55	76
3		0.052	27	7.4	0.28	0.17	0	8.1	1.3	490	440	0.45	444	370	28	72
4		0.079	40	9.2	0.58	0.33	0	8.2	1.3	330	408	0.42	417	420	44	100
5		0.083	42	8.5	0.40	0.25	0	8.1	1.3	390	353	0.41	355	500	31	66
6		0.039	50	4.2	0.26	0.15	0.81	6.4	3.2	370	342	0.65	458	1180	44	36
7		0.046	43	6.9	0.41	0.24	0.24	8.6	2.3	270	470	0.56	521	620	43	67
8		0.046	44	4.1	0.25	0.14	0.72	8.5	2.4	380	359	0.59	492	910	36	39
9		0.079	40	7.7	0.63	0.37	0.34	8.3	1.3	410	324	0.49	363	520	55	110
10		0.079	69	6.6	0.71	0.41	0.94	3.1	2.2	480	272	0.61	369	1060	74	71
11		0.079	70	7.2	0.63	0.37	1.00	3.1	2.2	430	275	0.63	387	970	62	63
12		0.083	54	10.0	0.87	0.65	1.1	3.3	2.1	320	331	0.77	556	650	70	113
13		0.092	83	12.0	0.44	0.26	0.98	3.1	2.3	300	356	0.77	604	670	27	37
14		0.092	77	12.0	0.39	0.24	1.1	3.4	2.1	320	404	0.75	645	660	26	36
15	Tertiary Butyl Mercaptan	0.050	22	5.8	0.34	0.21	0	9.4	1.1	340	388	0.42	390	380	39	107
16		0.077	31	8.3	0.47	0.29	0	10.1	1.0	370	360	0.43	362	350	38	107
17		0.082	107	21.0	0.44	0.26	0	9.0	2.2	290	484	0.47	491	610	16	43
18		0.124	55	13.0	0.87	0.54	0	8.9	1.1	330	349	0.48	352	380	42	110
19		0.148	82	21.0	0.47	0.26	0	7.7	1.4	290	391	0.42	394	440	15	36
20		0.050	63	7.7	0.79	0.45	0.97	3.4	3.1	260	375	0.70	659	860	77	88
21		0.077	70	12.0	0.56	0.32	0.97	3.2	2.3	260	415	0.83	760	590	35	56
22		0.077	95	9.8	0.69	0.40	1.1	3.6	3.1	310	393	0.84	725	990	45	51
23		0.088	83	13.0	0.51	0.30	0.55	8.6	2.3	280	437	0.65	579	650	31	43
24		0.124	106	19.0	0.67	0.40	1.0	3.5	2.2	260	412	0.83	779	550	25	44
						GROUP II										
25	Tertiary Dodecyl Mercaptan	0.090	43	10.0	0.47	0.27	0	8.9	1.1	360	374	0.41	383	430	33	76
26		0.090	78	9.5	0.64	0.38	1.0	3.1	2.2	380	313	0.69	456	690	49	57
27		0.090	74	8.5	0.35	0.21	1.1	3.5	2.1	350	281	0.68	414	400	29	33
28	Ethyl Mercaptan	0.015	19	1.8	0.29	0.17	0	6.4	3.7	320	405	0.42	407	1060	109	104
29		0.021	32	3.5	0.21	0.11	0	6.3	3.8	240	435	0.49	438	800	32	45
30		0.024	31	3.2	0.36	0.21	0	6.3	3.7	300	434	0.45	436	970	80	81
31		0.024	31	3.9	0.20	0.12	0	6.4	3.7	250	513	0.48	519	820	41	45
32		0.042	24	4.7	0.41	0.22	0	6.8	1.1	360	367	0.40	369	460	53	117
33		0.078	40	9.4	0.38	0.23	0	8.1	1.3	330	397	0.42	399	440	30	67
34		0.082	107	21.0	0.44	0.26	0	6.3	3.2	170	687	0.57	730	550	16	29
35		0.082	105	22.0	0.33	0.19	0	6.4	3.2	150	766	0.60	783	480	12	22
36		0.082	45	13.0	0.56	0.33	0	7.4	1.4	240	492	0.47	495	330	34	87
37		0.015	20	1.2	0.30	0.18	0.84	6.3	3.3	500	271	0.56	341	1610	178	108
38		0.022	29	1.9	0.42	0.25	0.80	6.3	3.8	450	283	0.58	363	1480	150	101
39		0.042	54	4.4	0.81	0.63	0.70	6.4	3.2	380	328	0.59	421	1230	128	105
40		0.046	105	8.6	0.12	0.07	0.60	3.1	5.7	210	539	0.80	820	1210	10	8
41		0.046	102	8.8	0.09	0.07	0.62	3.2	5.5	210	516	0.80	795	1160	9.8	8
42		0.078	71	7.1	0.47	0.34	1.0	3.2	2.2	440	267	0.65	387	950	58	62
43		0.082	130	10.0	0.72	0.42	0.78	6.4	3.2	320	369	0.72	531	1000	51	48

TABLE I Continued—SUMMARY OF TESTS OF A NICKEL CRACKING CATALYST

Run No.	SULFUR COMPOUND	SULFUR					OPERATING CONDITIONS			CONVERSION EFFICIENCY				CATALYST LIFE		
		Wt. % of Gasoline	Grains/CF Catalyst-Hr	Grains/CCF Reformed Gas	Pounds/CF Catalyst	Moles per Mole of Ni in Catalyst	Air/C Ratio	Steam/C Ratio	Gasoline Gal/CF-Hr	CF/Gal Gasoline	H V Btu/CF	Sp. Gr. Air = 1.0	N-Free H.V. Btu/CF	CF/CF Cat.-Hr.	Total MCF/CF Catalyst	Duration Hours
44	Hydrogen Sulfide	0.074	36	8.3	0.40	0.24	0	8.6	1.2	360	391	0.43	392	440	34	78
45		0.095	48	12.0	0.44	0.27	0	8.2	1.3	310	435	0.46	441	390	23	64
46		0.125	66	13.0	0.39	0.24	0	8.0	1.3	390	348	0.42	354	520	21	42
47		0.129	63	18.0	0.33	0.20	0	8.3	1.2	290	362	0.43	364	360	15	36
48		0.031	26	4.3	0.27	0.16	0.53	6.4	2.1	290	410	0.63	528	630	44	72
49		0.040	35	6.5	0.31	0.18	0.50	6.2	2.2	240	492	0.70	659	540	35	61
50		0.058	71	9.9	0.49	0.21	0.54	6.2	2.2	240	549	0.76	796	520	26	48
51		0.080	88	12.0	0.38	0.23	0.55	6.5	2.1	230	527	0.73	751	490	19	39
52		0.080	69	10.0	0.39	0.23	1.1	3.2	2.2	310	354	0.79	638	650	28	40
							GROUP III									
53	Normal Propyl Mercaptan	0.082	39	9.9	0.23	0.014	0	8.1	1.2	330	390	0.40	392	390	28	41
54		0.082	42	7.9	0.23	0.014	0	8.4	1.2	420	356	0.40	356	530	21	39
55		0.082	39	9.3	0.27	0.016	0	8.7	1.3	350	381	0.41	382	420	21	48
56	Dimethyl Sulfide	0.058	30	7.5	0.15	0.087	0	8.1	1.3	310	392	0.42	394	400	16	35
57		0.058	32	7.0	0.14	0.084	0	8.1	1.4	330	393	0.42	397	450	15	32
58		0.079	39	11.0	0.29	0.17	0	8.4	1.2	290	441	0.46	443	360	20	51
59		0.079	38	9.0	0.26	0.15	0	8.5	1.2	350	375	0.42	376	400	20	48
60		0.058	32	6.0	0.46	0.27	0.31	7.7	1.4	390	349	0.48	379	530	53	102
61	Diethyl Sulfide	0.083	41	13.0	0.30	0.18	0	9.1	1.3	260	480	0.48	487	330	17	50
62		0.083	71	9.8	0.35	0.21	1.0	3.3	2.4	330	340	0.78	564	700	29	34
							GROUP IV									
63	Tertiary Hexadecyl Mercaptan	0.035	19	4.1	0.15	0.089	0	7.9	1.3	320	386	0.43	386	430	25	56
64		0.046	23	4.9	0.10	0.071	0	8.4	1.2	380	357	0.40	358	450	18	37
65		0.046	23	4.9	0.10	0.061	0	8.4	1.2	380	340	0.40	352	450	16	32
66		0.128	64	19.0	0.14	0.082	0	8.4	1.3	280	462	0.44	464	350	5.2	15
67		0.035	17	3.5	0.19	0.11	0.33	8.6	1.2	420	329	0.50	334	500	38	78
68		0.035	47	4.0	0.87	0.051	0.78	6.2	3.3	340	343	0.66	470	1170	15	13
69		0.046	23	4.5	0.21	0.12	0.33	8.5	1.2	400	317	0.48	353	500	32	65
70	Thiophenol	0.068	34	7.2	0.11	0.063	0	8.2	1.3	375	375	0.42	389	475	10	22
71		0.068	35	7.7	0.089	0.052	0	8.2	1.3	350	360	0.41	364	450	8.1	18
72		0.068	34	8.2	0.17	0.10	0	8.2	1.3	330	386	0.44	390	440	16	35
73		0.068	33	7.0	0.51	0.30	0.34	8.4	1.2	390	341	0.49	374	480	49	106
74	Carbon Disulfide	0.080	41	16.0	0.23	0.11	0	8.1	1.3	200	409	0.49	411	260	11	31
75		0.080	38	8.9	0.51	0.30	0.27	8.7	1.2	360	355	0.51	396	400	38	95
76		0.080	72	12.0	0.42	0.24	0.98	3.1	2.3	270	369	0.78	639	610	27	41
77		0.080	67	9.4	0.18	0.11	1.1	3.3	2.1	340	350	0.75	572	710	14	19
78		0.080	67	9.9	0.10	0.06	1.1	3.4	2.1	330	365	0.74	588	670	7.4	11

TABLE II—SUMMARY OF TESTS OF NICKEL SULFIDE CRACKING CATALYSTS

Run No.	Catalyst	Hydrogen Sulfide: IN Grains/CF	Hydrogen Sulfide: OUT Grains/CF	Operating Conditions: Natural Gas CF/CF Cat-Hr	Operating Conditions: Steam/C Ratio	Operating Conditions: Mid-Tube Wall Temp. °F	Operating Conditions: Duration Hours	Gas Analysis: CO_2	Gas Analysis: H_2	Gas Analysis: CO	Gas Analysis: C_nH_{2n+2}	Gas Analysis: N_2	Conversion Efficiency: CF CF Natural Gas	Conversion Efficiency: CF CF Catalyst-Hr.	Conversion Efficiency: H V Btu/CF	Conversion Efficiency: Sp. Gr. Air = 1.0	Conversion Efficiency: % Conversion
	CATALYSTS BASED ON POROCEL CARRIER																
1	100% Porocel	3900	3900	100	3.2	1450	7	2.8	44.9	7.2	40.0	5.1	1.71	170	564	0.42	35
2		3900	3900	210	3.7	1450	6	2.2	33.5	5.3	50.0	9.0	1.49	290	621	0.47	30
3		3900	3900	47	2.6	1450	5	2.4	44.4	4.8	42.3	6.1	1.69	80	578	0.41	32
4		3900	3900	29	3.6	1450	6	2.3	42.3	5.2	43.4	6.8	1.7	50	583	0.42	29
5		3900	3900	160	4.8	1700	5	6.5	58.4	10.8	19.7	4.6	2.88	460	417	0.40	47
6		3900	3900	260	4.7	1700	6	3.3	56.0	11.0	24.6	5.1	2.56	660	458	0.38	40
7		3900	3900	320	3.8	1700	5	3.1	55.5	11.3	24.7	5.4	2.55	810	459	0.39	40
8		3900	3900	110	3.8	1700	5	4.4	63.0	11.5	17.0	4.1	2.98	320	407	0.36	52
9	5.6% Ni_3S_2 — 94.4% Porocel	3650	3300	39	4.3	1470	10	18.2	63.2	2.6	11.1	4.9	2.75	110	320	0.43	72
10		3650	3300	22	4.3	1500	10	14.0	61.1	1.6	18.0	5.2	2.8	62	382	0.43	52
11		7600	8150	21	4.5	1490	7	11.2	53.8	2.3	28.6	4.1	2.7	60	463	0.43	28
12		7600	7600	20	4.9	1490	7	9.6	39.9	2.0	41.5	7.0	2.1	44	547	0.49	21
13		7600	7900	21	4.5	1490	7	3.1	11.2	0.3	76.3	9.1	1.4	29	813	0.58	0
14		3650	3650	22	4.0	1510	5	3.8	36.6	1.9	50.8	6.9	1.8	40	655	0.47	10
15		3650	3650	20	4.4	1510	5	3.9	36.1	1.8	51.1	7.1	1.8	37	656	0.47	9
16	5.5% Ni_3S_2 — 94.5% Porocel	3000	3000	75	2.6	1490	4	9.6	41.3	2.1	42.0	5.0	2.05	150	556	0.74	21
17		3000	3000	22	4.9	1490	4	11.1	53.7	2.2	28.7	4.3	2.6	57	464	0.43	34
18		3300	3350	45	1.9	1475	8	9.2	41.9	2.8	40.9	5.2	2.0	90	549	0.47	24
19		—	—	23	4.0	1465	10	13.4	62.5	3.2	14.9	6.0	3.2	73	358	0.42	56
20	6.0% Ni_3S_2 — 0.1% Al_2O_3 — 93.9% Porocel	3900	3900	28	3.6	1450	5	11.6	66.0	12.0	7.0	3.4	3.4	98	318	0.41	78
21		3900	3900	45	4.2	1450	5	10.1	61.4	12.3	12.9	3.3	3.11	140	363	0.42	63
22		3900	3900	180	4.5	1450	5	11.2	44.8	4.2	34.0	5.8	2.13	390	495	0.49	33
23		3900	3900	175	5.3	1700	10	9.5	65.4	12.6	8.9	3.6	3.43	600	337	0.38	72
24		3900	3900	340	3.4	1700	6	8.1	54.7	6.3	26.2	4.7	2.63	900	455	0.41	36
25		3900	3900	230	4.3	1700	6	3.2	61.5	11.3	20.3	3.7	3.12	730	434	0.35	42
26		3900	3900	92	5.7	1700	6	10.0	68.0	9.4	9.6	3.0	3.73	340	342	0.37	67
27		1800	1800	170	5.5	1700	5	9.1	66.5	12.8	9.1	3.5	3.45	570	340	0.39	71
28		1800	1800	170	5.5	1700	5	9.0	65.6	12.6	9.2	3.6	3.44	570	341	0.39	71
29		1300	1300	170	5.4	1700	5	10.4	64.3	10.6	10.8	3.9	3.23	540	346	0.40	68
30		850	850	170	5.6	1700	7	8.4	63.3	7.6	16.9	3.8	3.19	530	394	0.38	50
31		3000	3000	170	5.3	1700	6	10.0	65.0	11.1	10.2	3.7	3.49	605	344	0.40	67
32		610	610	160	5.9	1700	6	8.0	55.4	6.4	25.4	4.8	2.72	430	450	0.41	36
33	6.1% Ni_3S_2 — 0.3% Al_2O_3 — 93.6% Porocel	3300	3300	24	3.8	1470	8	12.1	71.0	11.1	3.2	2.6	3.7	89	294	0.39	89
34		3300	3400	51	2.4	1470	6	11.0	69.4	7.2	9.6	2.8	3.19	165	340	0.37	72
35		3300	3300	190	4.3	1450	7	9.6	45.8	2.4	38.0	4.2	2.00	385	532	0.45	30
36		3300	3300	115	3.1	1450	8	10.7	56.9	3.7	23.3	5.4	2.75	320	425	0.43	41
37		3300	3400	35	3.7	1450	5	10.8	68.2	9.4	8.5	3.1	3.2	110	332	0.38	75
38		3300	3300	24	3.6	1455	6	12.3	70.3	11.8	3.0	2.6	3.8	93	290	0.39	89
39		3300	3300	24	2.3	1450	6	12.6	67.5	7.4	9.5	3.0	3.7	89	331	0.39	88
40		3300	3300	24	0.71	1455	6	9.7	44.9	2.6	38.3	4.5	2.0	49	537	0.46	27
41		1800	<2000	25	3.7	1455	10	11.4	61.5	4.0	19.7	3.4	3.1	77	403	0.40	43
42		1200	<1600	25	4.0	1460	10	11.6	61.5	3.7	19.9	3.3	3.0	76	404	0.40	45
43	6.0% Ni_3S_2 — 0.5% Al_2O_3 — 93.5% Porocel	4900	4900	39	3.6	1450	5	5.8	77.2	12.9	1.6	2.5	4.0	160	301	0.30	94
44		4900	4900	275	4.4	1450	5	2.2	51.2	9.8	32.8	4.0	2.40	660	519	0.39	27
45		4900	4900	36	3.9	1450	5	6.0	70.0	10.5	11.1	2.4	3.9	140	365	0.33	60
46		4900	4900	180	3.0	1450	5	2.2	59.6	12.4	21.4	4.4	3.54	625	441	0.36	30
47		2300	2200	33	4.2	1450	10	12.9	64.2	2.9	14.4	5.6	3.45	110	355	0.41	54
48		2300	2200	30	2.1	1450	10	11.6	59.0	2.8	21.5	5.1	3.0	89	409	0.41	41
49		3900	3900	45	4.7	1700	4	5.5	74.0	15.9	2.6	2.0	4.4	200	312	0.32	89
50		3900	3900	140	4.4	1700	5	6.2	70.5	11.4	9.0	2.9	3.92	540	351	0.33	86

TABLE II Continued—SUMMARY OF TESTS OF NICKEL SULFIDE CRACKING CATALYSTS

Run No	Catalyst	Hydrogen Sulfide: IN Grains/CF Catalyst-Hr.	Hydrogen Sulfide: OUT Grains/CF Catalyst-Hr.	Operating Conditions: Natural Gas CF/CF Cat.-Hr.	Operating Conditions: Steam/C Ratio	Operating Conditions: Mid-Tube Wall Temp. °F	Operating Conditions: Duration Hours	Gas Analysis: CO_2	Gas Analysis: H_2	Gas Analysis: CO	Gas Analysis: C_nH_{2n+2}	Gas Analysis: N_2	Conversion Efficiency: CF/CF Natural gas	Conversion Efficiency: CF/CF Catalyst-Hr.	Conversion Efficiency: H.V. Btu/CF	Conversion Efficiency: Sp. Gr. Air = 1.0	Conversion Efficiency: % Conversion
51	6.1% Ni_3S_2 — 1.1% Al_2O_3 — 92.8% Porocel	3500	3500	25	3.9	1455	10	12.9	70.5	12.2	1.4	3.0	4.0	100	278	0.40	95
52		3500	3500	52	7.0	1450	5	10.4	66.1	9.6	10.5	3.4	3.51	180	346	0.39	66
53		3500	3500	100	3.5	1450	5	2.5	61.7	12.1	20.0	3.7	2.99	310	435	0.35	45
54		3500	3500	210	3.9	1450	8	2.0	53.1	10.3	30.7	3.9	2.41	515	508	0.38	32
55	6.0% Ni_3S_2 — 6.2% Al_2O_3 — 87.8% Porocel	3900	3900	27	3.7	1450	6	6.2	70.0	11.3	10.3	2.2	3.7	100	362	0.33	65
56		3900	3900	55	3.7	1450	6	12.0	65.3	3.3	14.9	4.5	3.28	180	367	0.39	55
57		3900	3900	110	3.9	1450	6	3.0	56.8	12.0	22.8	5.4	2.84	310	446	0.38	40
58		3100	3100	25	4.5	1450	8	8.4	63.9	7.5	16.8	3.4	3.25	81	395	0.37	50
59	3.0% Ni_3S_2 — 0.5% Al_2O_3 — 96.5% Porocel	3900	3900	100	4.1	1450	5	8.1	55.4	6.5	25.3	4.7	2.64	270	449	0.41	38
60		3900	3900	49	4.2	1450	6	7.2	61.8	7.1	20.1	3.8	3.18	150	420	0.37	43
61		3900	3900	25	4.8	1450	6	9.0	65.5	12.7	9.4	3.4	3.3	84	343	0.39	71
62		3900	3900	240	4.8	1700	5	9.1	65.2	13.0	9.0	3.7	3.31	800	339	0.40	73
63		3900	3900	330	4.2	1700	5	10.1	61.5	10.4	14.1	3.9	2.91	950	370	0.41	61
64	10.0% Ni_3S_2 — 0.5% Al_2O_3 — 89.5% Porocel	3900	3900	28	3.9	1450	5	9.9	67.8	9.3	9.9	3.1	3.7	105	344	0.37	66
65		3900	3900	48	4.5	1450	6	11.5	65.4	3.9	15.0	4.2	3.56	170	370	0.38	51
66		3900	3900	190	4.0	1450	6	3.2	49.8	9.0	33.6	4.4	2.35	460	522	0.40	27
								MISCELLANEOUS CATALYSTS									
67	22.4% Ni_3S_2 — 77.6% Al_2O_3	1700	1900	95	0.8	1120	1	0.2	0.3	0.0	89.8	9.7	1.00	95	960	0.64	8
68		1700	1900	60	1.0	1115	3	1.2	2.4	0.1	86.7	9.6	1.05	64	928	0.63	8
69		1700	1900	32	0.9	1110	3	2.2	4.3	0.1	83.6	9.7	1.15	37	897	0.63	2
70		2300	2800	20	1.9	1140	6	—	—	—	—	—	1.8	36	—	—	—
71		0	1000	22	1.8	1120	12	3.3	36.1	3.6	47.2	9.5	1.7	36	633	0.48	21
72		0	300	23	1.9	1095	8	3.0	33.2	3.3	51.0	9.5	1.8	41	647	0.49	9
73		2400	2700	23	1.9	1465	11	9.5	39.8	1.1	39.8	9.8	2.1	48	526	0.50	22
74	Ni on $ZrSiO_3$ (dense)	3300	3300	34	2.7	1450	6	3.0	10.6	0.2	77.1	9.1	1.3	42	835	0.59	6
75		3300	3300	19	4.8	1450	6	2.3	9.8	0.2	78.5	9.2	1.3	24	859	0.60	5
76	Ni on $ZrSiO_3$ (porous)	3900	3900	27	4.1	1445	6	6.6	52.4	11.0	25.0	5.0	2.55	70	451	0.43	41
77		3900	3900	44	4.7	1450	6	7.6	48.0	8.0	29.7	6.7	2.28	100	474	0.46	37
78		3900	3900	79	4.4	1450	4	7.8	34.3	13.3	38.3	6.3	1.82	145	533	0.55	36
79		3900	3900	130	5.9	1450	4	5.9	31.3	2.3	53.9	6.6	1.82	235	644	0.50	10
80	Ni on $NiAl_2O_4$	3900	3900	25	4.2	1450	10	10.5	67.4	9.5	9.5	3.1	3.6	91	340	0.36	68
81		3900	3900	110	2.9	1450	13	10.7	67.2	9.6	9.4	3.1	3.60	390	338	0.36	69
82		3900	3900	140	3.2	1450	5	10.3	65.2	9.7	11.6	3.2	3.32	465	354	0.39	64
83		3900	3900	240	3.9	1450	5	5.1	36.5	3.9	49.0	5.5	1.80	430	615	0.47	18
84	Commercial Ni Catalyst	3300	2400	24	3.8	1450	5	3.0	15.1	0.4	72.5	9.0	0.7	17	835	0.59	47

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RESEARCH BULLETIN

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INSTITUTE OF GAS TECHNOLOGY
RESEARCH BULLETIN
11

EXPANSION BEHAVIOR OF COAL DURING CARBONIZATION

A Literature Study

by

O. P. Brysch
W. E. Ball

Sponsored by

THE GAS PRODUCTION RESEARCH COMMITTEE

of the

AMERICAN GAS ASSOCIATION

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PREFACE

This bulletin, the eleventh in a series, presents the results of a critical review of the literature made in the libraries of the Institute of Gas Technology on the expansion behavior of coal during carbonization, and a survey of industrial practice made by members of the Institute staff to determine the present state of the art of coal carbonization. This work was undertaken as a result of the action of a project Formulation Subcommittee of the American Gas Association's joint Subcommittee on Stresses and Strains. This Committee, on May 17, 1949, moved that "a program of research be instituted as promptly as possible and that formal request be made to the proper authorities to implement this program; a critical review of the present state of the art (be made) by a qualified agency, including literature and present practice within the industry and (that this agency) make recommendations of future studies on fundamental problems of coal carbonization".

Anticipating the action of the Formulation Subcommittee, the Institute of Gas Technology initiated a literature search in February, 1949, as a part of the Institute's basic research program. In October, 1949, the Gas Production Research Committee of the American Gas Association sponsored the continuation of this study as "Coal Expansion during Carbonization," Project PB-1, under the PAR (Promotion-Advertising-Research) Plan. The project plan provided that a literature survey and review of industrial practice would be followed by a critical analysis of the material obtained with the major objective of formulating the most promising plan of research for determining the factors involved in the expansion of coal during carbonization. It was hoped that these factors could be successfully correlated with comparatively simple laboratory tests and that these tests could then be substituted for the more difficult and costly method of large-scale pilot-oven testing. Thus, the ultimate research objective was to develop a sound method of predicting expansion behavior during carbonization from laboratory measurements of fundamental coal properties.

The literature containing several thousand contributions on carbonization and on the coking properties of coal and coal blends was reviewed, and some two hundred references dealing with the expansion behavior of coals, including the comprehensive review of this subject through 1940 made by Brewer, were abstracted and studied. In this study, emphasis was placed on the more recent literature believed to contain the more valuable data. In addition to the published literature, data on bulk densities were obtained from two Masters' theses, and on the heat of wetting of selected coals from a third Master's thesis, at the Institute of Gas Technology.

Methods of expansion pressure control in the coke oven industry were studied during personal visits to three typical plants. The remainder of the data on industrial practice was obtained from the published literature. An attempt was made to include all published methods of expansion control. It is known, however, that a few plants use special methods, the details of which have not been published.

The authors wish to gratefully acknowledge the guidance and assistance of the Project Supervising Committee, of the Gas Production Research Committee, and of Mr. T. L. Robey and Dr. N. K. Chaney of the American Gas Association staff.

E. S. PETTYJOHN, *Director*
Institute of Gas Technology

Chicago, Illinois
October, 1951

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ABSTRACT

Of the voluminous literature on coal carbonization and coal properties, in excess of seven hundred references have been scanned, and some two hundred references, of special significance to the factors involved in the expansion behavior of coal during carbonization and the origin, magnitude and measurement of the expansion pressures developed by coals and coal blends, have been critically reviewed. A summary of the more significant findings and opinions appears in the body of this report. This literature survey has been supplemented by first-hand inspection of current coke oven practice in modern plants.

A special study and analysis has been made of possible correlations between expansion pressures developed during carbonization and the properties of coal which were measured in the laboratory. From such correlations it was hoped that a definite and scientific prediction could be made of the anticipated expansion behavior during carbonization, to assist the operator in the selection and blending of coals for his oven charges, rather than the current more costly and time-consuming pilot-oven tests. The conclusion was reached that while none of the correlations hitherto attempted permit coke oven behavior to be predicted from laboratory determinations of coal properties, nevertheless, attainment of this goal is within the possibilities of further intensive research.

To this end a concrete research proposal is outlined, the essential feature of which is the procurement of an adequate series of representative coals of known expansion behavior and coking properties, especially those coals of similar chemical composition but of different known expansion behavior, as predetermined in Russell oven tests and plant use by cooperating coke producing companies. The physical properties of this series of coals will be exhaustively studied by existing laboratory techniques, and the internal structure will be studied by newly developed procedures using the latest in laboratory equipment. If no successful correlations can be found, further research is proposed to develop new methods for the direct measurement of the rates of gas evolution and the resistances to gas escape believed to be the primary causes of coal expansion pressures.

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THE PROBLEM

The economic operation of coke ovens is of direct importance not only to members of the utility gas industry, which operate their own plants, but also to those which purchase coke oven gas, or purchase coke for gas manufacture. Refinements in oven design have resulted in increased speed and efficiency, and structures have necessarily become more complex and expensive. The shortages of material and labor and the cost of repairs under present conditions re-emphasize the necessity for the reduction or prevention of damage to oven walls at present-day higher operating rates.

Although it is known that other causes contribute to premature wall failure, certain types of damage have been traced directly to excessive expansion pressures developed during carbonization. The prevention of damage from excessive expansion pressures has been the subject of extensive investigation for many years. Most of this work has been of a practical nature. Investigations have been made to determine the effects of varying operating conditions in commercial plants, and to assess the comparative expansion characteristics of coal charges by direct tests in pilot ovens. Under pressure of national emergencies and because of the depletion of some of our best coking coals, the importance of testing coal expansion has greatly increased in recent years. Unfortunately, the large-scale oven methods which are believed to be most reliable are costly and time consuming as compared with ordinary laboratory tests.

As a consequence, there has been more than an academic interest in recent research on the causes of expansion pressures during carbonization, and in the tentatively proposed attempted correlations between the properties of coal and its expansion behavior. Although none of these correlations have been developed to the point where expansion behavior can be accurately predicted from measurements of coal properties, work of this type has shown considerable promise. Difficulties have understandably been encountered due to inadequate knowledge of a more fundamental nature regarding the structure of coal and the mechanism of carbonization.

The problem is, therefore, through a critical review of the literature and industrial practice to present the state of the art of coal carbonization, and to recommend a comprehensive program of research directed toward establishing the fundamental factors governing the expansion behavior of coals and coal blends during carbonization.

CONCLUSIONS

I. Conclusions Based Upon the Present State of the Art

From the critical review of the literature and industrial practice, the following findings and conclusions are drawn:

1. Occurrence and Control of Expansion Pressures

Coke may be defined as "the coherent, cellular residue from the destructive distillation of certain bituminous coals". The volumetric expansion of the coal particles during carbonization accompanied by expansion pressures must be accepted as necessary to the production of strong, well-fused coke. However, excessive volumetric expansion or excessive expansion pressure will accelerate the normal rate of deterioration of oven walls. Hence, methods of controlling expansion pressure must be employed, the more usual of which include:

a. Blending of expanding coals with contracting coals.

b. Bulk density regulation, by varying the particle size and size distribution, adjustment of moisture content, and addition of oil.

c. Addition of inert materials, such as anthracite fines, low- and high-temperature coke breeze, and oxidized coals.

d. Addition of pitch to reduce the expansion of low-volatile coals, and to enhance the coking properties of low-rank coals.

e. Control of the rate of heating.—Decreasing the rate of heating usually lowers the expansion pressure.—This factor also permits varying the blend to accommodate different oven widths.

2. Measurements of Expansion Pressures

The methods of control listed are applicable only within relatively narrow limits. The results are difficult to predict, since the variables involved are often mutually dependent. Consequently, selection of proper blend proportions and of operating conditions requires extensive testing in pilot ovens.

Large-scale test ovens have, over a period of years, demonstrated their adequacy in determining the relative expansion behavior of coal charges. The more commonly used are:

a. The Russell movable-wall oven, heated from two sides, for determining expansion pressure at constant volume.

b. The Brown-type sole-heated oven, for determining volumetric expansion and contraction at constant pressure.

Reduction of such testing techniques to bench-scale or laboratory expansion testing methods has yielded either incomplete or misleading results.

3. Fundamental Determinants of Expansion Pressures

A critical analysis of the development of expansion pressures shows that the fundamental determinants involved are two:

Rate of gas evolution

Resistances to the escape of gas.

The significant resistances to the escape of gas are:

a. The capillary structure—which governs the swelling of individual coal particles.

b. The plastic layer—which determines the pre-peak pressure.

c. The plastic envelope—which governs the peak pressure.

The problems of directly measuring the rate of gas evolution and of determining the values of the resistances by laboratory methods which would simulate coke oven conditions remain to be solved. None of the various coal properties or parameters of physical measurement have as yet provided satisfactory correlations with oven tests as means of predicting expansion pressures.

Since it is of paramount importance to the coking industry that the dwindling supply of premium coking coal be effectively utilized, increased knowledge of the expansion behavior of coal during carbonization, and simpler and more accurate methods of predicting such behavior, based on laboratory tests for chemical and physical properties of coal and coal blends, are sorely needed.

II. Recommended Program of Research

The critical review of the research findings and of the practical experience described herein has led to the conclusion that the following research program offers a reasonable and practical approach to the solution of the Problem:

OBJECT—To develop correlations between 1) the known expansion behavior and coke quality, and 2) the chemical and physical properties of coals and coal blends, to permit the prediction of expansion behavior from simple inexpensive laboratory tests.

PLAN A.—Representative samples of types of coals and coal blends with known expansion behavior as determined by actual Russell movable wall pilot-oven tests, and of coke quality from plant operation, will be obtained from cooperating companies. These selected coals and coal blends will be subjected to accepted chemical and physical tests such as proximate and ultimate analysis, free swelling index, fluidity by Gieseler plastometer, x-ray diffraction, and other tests. The internal structure of the particles of these same coals and coal blends will be measured by one or more of the following methods:

a. Internal surface area (by Brunauer-Emmett-Teller surface area measurement procedure).

b. Porosity (computed from the true and apparent specific gravities).

c. Heats of wetting of the coal particles by various solvents.

d. Moisture absorption (from the determination of equilibrium moisture content at varying relative humidities and the saturated and air dried moisture contents).

An attempt will then be made to correlate the data from the laboratory tests with the pilot-oven and plant results, both as to expansion behavior and coke quality. Thus, by starting with groups of coals of pre-determined expansion behavior, the presence or absence of any correlation between 1) accepted chemical and physical tests, and 2) internal structure, with 3) expansion behavior and coke quality, will be immediately evident. To the extent that useful correlations can be found, they will provide the desired means of predicting the expansion behavior of coal and coal blends in advance of the slower and more costly oven tests.

PLAN B.—In the event the testing procedures outlined above do not provide satisfactory correlations, it will be necessary to develop new tests of a kind which for the reasons discussed herein may be expected to show the desired correlations. These tests will include direct means for measuring 1) the rates of gas evolution as the coal is heated, and 2) the permeability of the plastic layer and plastic envelope, or alternatively, 3) some means of measuring coal viscosity at elevated temperatures—using pressure to retard destructive distillation. The basic starting point for the development of these new tests would remain the same as for the initial work, namely, the existence of a series of representative examples of typical coals and coal blends of predetermined expansion behavior and coking properties upon which the utility of the new techniques can be effectively tested.

For the initial tests in Plan A above, a reasonable survey could be accomplished in approximately one year. An extension of this approach to additional coals and to other locations might take substantially longer.

The development of methods of measuring rates of gas evolution and the permeability of the plastic layers involve a time element which cannot be estimated at this time.

DISCUSSION

The problem in the selection of coals for control of expansion pressure during carbonization is not one of distinguishing between coals of different rank or of widely different chemical compositions as measured by proximate and ultimate analyses, but is one of differentiating between coals of the same rank and apparently identical chemical compositions which exhibit widely divergent expansion behaviors.

I. Inadequacy of Existing Correlations Between the Expansion Behavior and the Properties of Coal

Attempts to correlate expansion behavior with physical and chemical properties of the coal have met with only limited success. For example:

a. There are specific cases in which expansion decreases as volatile matter increases, indicating that volatile matter may function more as an inverse indication of resistance than as a direct indication of rate of gas evolution.

b. Severe limitations attend the use of Gieseler fluidity to indicate the resistance offered by the plastic envelope to the flow of gas (permeability). The expected inverse relationship between fluidity and expansion pressure holds only for the medium-volatile and certain of the low-volatile coals. Coals at the limits of the coking band, and oxidized and high-inert charges exhibit both low fluidity and low expansion pressure. Fluidity criteria are of limited application to blends, since high-volatile coals of either high or low fluidity will decrease the expansion pressures of low-volatile coals.

c. In the absence of other information concerning physical structure, reliance has necessarily been placed upon various moisture criteria. The expansion pressures of binary blends were found to be more closely related to the air-dry moisture of the high-volatile coal than to any other factor. Similarly, the volume expansions of blends were found to be primarily a function of the expansion (usually negative) of the high-volatile coal, which in turn was found to be a function of volatile matter and air-dry moisture.

The inclusion of various moisture criteria in expansion correlation and coal classification is proof of the importance of physical structure. However, presently employed moisture methods for obtaining information about physical structure have the following disadvantages:

a. Total moisture is not representative of bed moisture on as-received samples.

b. Air-dry moisture is not a definite quantity, because of dependence upon ambient temperature and humidity, and other factors.

The selected measures (volatile matter, fluidity and moisture) have given only indirect measurements of the resistances (of the capillary structure, plastic layer and plastic envelope) encountered and have shown either approximate or limited relationships. Although the correlations presented between expansion behavior and coal properties leave much to be desired, the relationships are much closer than would be expected from the laws of chance, particularly when errors of measurement are taken into consideration. The reason that these correlations have not been completely successful in predicting expansion over the whole range of coals and coal blends is that the coal properties selected are inadequate indications of the following two fundamental properties, namely:

Rate of gas evolution.
Resistances to the escape of gas.

II. Study of New Methods and New Correlations

The more promising approaches to the problem of relating expansion behavior to coal properties would seem to depend either on the finding of more precise means of predicting their effects from other coal properties, which can be measured by existing methods, or on the development of new methods of measuring these two fundamental properties directly.

III. Relationship of Permeability to Fluidity and Swelling

Research should be directed toward ascertaining the causes for differences in permeability. For unblended coals, there is evidence of a relationship between permeability and fluidity over limited ranges, the irregularities being credited to a discontinuity of the plastic layer due to insufficient swelling of the coal particles. Attempts currently in progress to improve the Gieseler plastometer should eventually lead to more satisfactory measurements of fluidity.

To measure the swelling of coal particles is a difficult problem. The only swelling method presently accepted is the free-swelling index. This may not prove to be directly applicable to swelling during carbonization because of the rapid rate of heating used. A dilatometer test, as for example some modification of the Agde-Damm procedure, may offer a better approach.

On the other hand, since swelling of individual particles is so difficult to measure, measurement of the resistances (or forces) involved in swelling may be preferable.

For blended coals, a determination of the temperature ranges of fluidity and of the free-swelling index of the constituent coals may permit a prediction of the resulting permeability.

IV. Relationship of Swelling to Internal Structure

The theory of Berkowitz, that coking properties are closely related to physical structure, should be further investigated. Knowledge of physical structure may be useful in predicting swelling behavior, particularly for high-volatile coals, thus making it possible to relate physical structure directly to permeability. Precise measurement of the absolute surface areas may be obtained by calculation from adsorption isotherms observed by use of the Brunauer-Emmett-Teller apparatus. It may also be possible to substitute for the above the relative surface area obtained by the comparatively simple method of heat of wetting.

The standard methods for obtaining indirect information concerning the physical structure of coal are the total and air-dry moisture contents, the limitations of which have been mentioned. For these measures, the porosity as calculated from true and apparent densities may perhaps be substituted. Also, the measurement of the amount of moisture adsorbed at standard humidity and temperature may prove to be satisfactory.

V. Relationships Between Physical Properties and Chemical Analysis

Since it has been shown that some degree of relationship exists between physical properties, such as softening and swelling, and the proximate and ultimate analysis, it is possible that further simplification of expansion testing may be achieved by relating the chemical analysis to physical properties, which may be more easily correlated, and to expansion behavior.

Some progress has been made by Russell and Brewer in relating fluidity to proximate analysis, and by Mott in correlating swelling properties and agglutinating value with ultimate analysis. The collection of more comparative data on these properties, including permeability, on groups of chemically similar coals, may permit a better interpretation of the influence of chemical composition upon coking behavior.

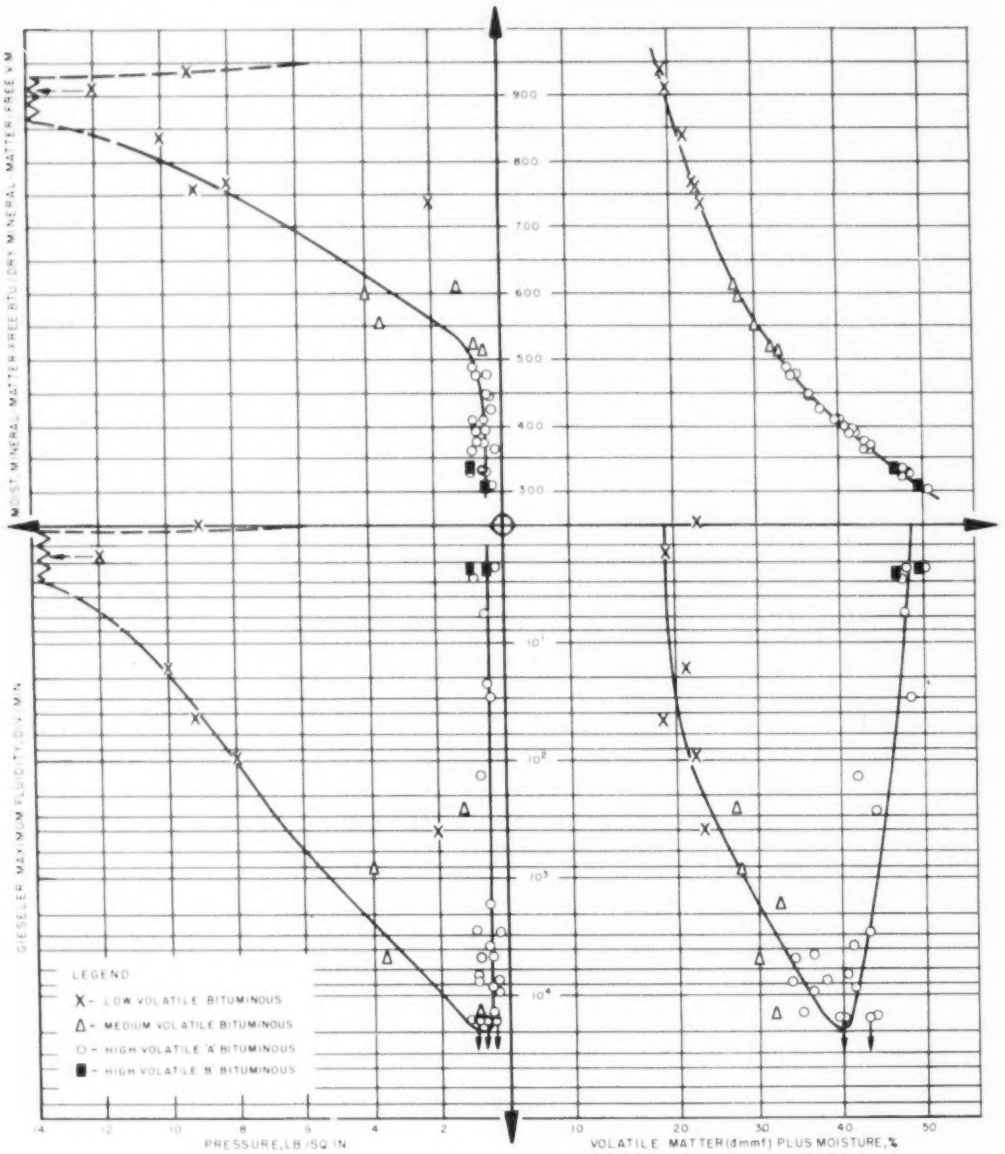

Fig. 1-S. INTER-RELATIONSHIPS OF EXPANSION PRESSURE, COAL RANK, AND GIESELER FLUIDITY

(Data from Russell and Perch)[167]

SUMMARY

I. Damage to Oven Walls

Among the recognized causes for premature failure of coke oven walls are: distortion and destruction by the expansion pressure of the charge, disruptive forces exerted by the pusher when there has been insufficient contraction of the charge, thermal shock of wet coals, too-rapid heating or cooling schedules, slagging action of mineral matter, and cooling of the ends by delaying the replacement of doors.[75, 84] This report is concerned with the first two causes, those due to expanding coals.

II. Mechanism of Carbonization

The generally accepted theory for the carbonization of particulate coal is that the influence of heat causes the particles to soften, swell, and devolatilize, and that these processes must be accompanied by sufficient pressure to deform the swollen particles into a coherent mass. In the ordinary coking process, the pressure results from the weight of the superincumbent coal, and from the restraining of gases of decomposition by the coal particles, plastic layers, or plastic envelope. Excessive pressure is of course undesirable, because of its effects upon oven walls. These processes of softening, swelling, and devolatilization occur simultaneously, but will be considered separately to the extent that is possible.

A. Softening. The effect of heat in causing the transformation of coal from the solid to the plastic state has been ascribed to the increased rate of oscillation of molecules or atomic groups at the micellar surfaces at higher temperatures, with a resulting decrease in the intrinsic strength of the coal.[19] The change with temperature in fluidity of the pulverized coal mass has been measured with torsional plastometers, usually of the Gieseler type. Russell has shown the characteristic relationship between coal rank and plasticity as measured with the Gieseler plastometer for typical coals to be:[167]

Typical Coal		Plastic Temperature Range, °C		
Rank	Volatile Matter %	Initial Fusion	Maximum Fluidity	Solidification
Low-Volatile	17	440	480	500
Med.-Volatile	22	395	475	505
High-Volatile	34	370	450	480
High-Volatile	38	380	440	465

The relationship between maximum fluidity and coal rank is shown in Fig. 1-S.[167] Other factors which influence the fluidity include:

1. Decreasing the rate of heating shortens the temperature range of plasticity and decreases the fluidity.[113, 167]
2. Oxidation of the coal has a similar effect.[167]
3. High concentrations of anthraxylon, translucent attritus and cannel coal increase the fluidity.[20]
4. High concentrations of ash, opaque attritus, and fusain decrease the fluidity.[20]

The relationship between maximum fluidity and expansion pressure is also shown in Fig. 1-S. Most of the low-, medium-, and higher-ranking high-volatile coals show the expected inverse relationship between fluidity and expansion pressure. The coals at the limits of the coking band are anomalous in that they show both low fluidities and low expansion pressures. It is probable that the swelling of the latter coals is insufficient to form continuous plastic layers.

B. Rate of Volatilization. The change in rate of volatilization of typical coals as the temperature is increased is shown in Fig. 2-S.[155] The regions of maximum rates of gas evolution correspond with those of maximum fluidity. Comparison with expansion pressure curves of the coal indicated that expansion pressure was due to the liberation of relatively large amounts of volatile matter while the coal mass was in a viscous condition. While these relationships have been used to make qualitative predictions of expansion pressure,[155] the interpretation is difficult, and some investigators[111] have not been able to correlate data of this kind with expansion pressure.

C. Swelling vs. Internal Structure. Berkowitz has explained the swelling of coals by reference to their internal structures.[19] Recent research[56] conducted in England on the physical structure of coal indicates that coal is built up of aggregates of molecules (micelles) separated by capillaries, whose average diameter is of the order of 40 angstroms. The absolute surface areas of these capillaries as calculated from adsorption isotherms have been reported for only a few coals. More

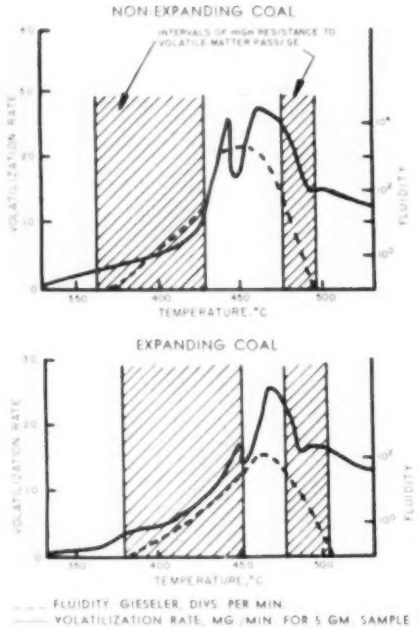

Fig. 2-S. Fluidity-Volatilization Relationships[185]

complete data (Fig. 3-S) are available showing the relative surface areas, as determined by heat of wetting in methanol, for coals of various volatile matter content.[77a]

The volume of the capillary spaces has been estimated from measurement of the true and apparent densities.[50] When porosity was plotted against volatile matter (Fig. 4-S), the same type of curvature was shown as for surface area.

Since coals in the natural condition contain moisture adsorbed on the capillary surfaces, it would be expected that moisture content curves would resemble those observed for surface area and porosity. The similarity is evident, whether moisture is reported on the total,[141] air-dried, or 50% humidity[150] moisture basis. Fig. 5-S shows the relationship which has been observed between heat of wetting and air-dried moisture.[77a]

Measurements of apparent densities[64, 65] and of heats of wetting[27, 120] of coals and chars showed "drifts" of density with time, and variations in heats of wetting, which could be accounted for only by the presence in the capillaries of constrictions, of diameters approximating those of simple molecules (2 to 5 angstroms). It was also observed that these constrictions were present most often in the coking coals.

From this observation it would appear that the poorly-coking and non-coking coals are characterized by a comparatively open type of capillary structure, whether judged by surface area, porosity, or constrictions. Studies of the internal structures of coals and their cokes produced at different temperatures showed that capillarity persisted throughout carbonization, and therefore complete fusion of the coal did not take place.[65, 120]

According to the theory of Berkowitz, the swelling of particles of coking coal is due to the entrapment of gases of decomposition within the capillary structure described.[19] The rate of diffusion of these gases to the exterior of the particle will be governed by the pore diameter and constrictions. In the case of the coking coals, the restrictive nature of the capillary structure causes a build-up of gas pressure within the pores. As the temperature is increased, the coal softens, and the pressure of the interior gases distends the particle. In confirmation of this theory, tests have shown that slow rates of heating (0.5 C per min.) will greatly suppress swelling, and rapid rates will produce coke-like residues from normally non-coking coals.

Mott,[127] by measurement of the swelling of individual coal particles, showed that the coking coals are characterized by high percentages of

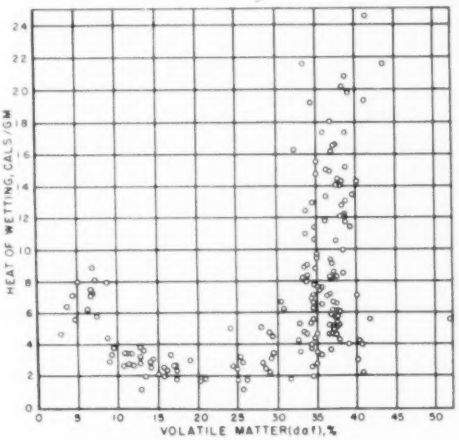

Fig. 3-S. The Heats of Wetting of Coals of Differing Volatile Matter Contents[77a]

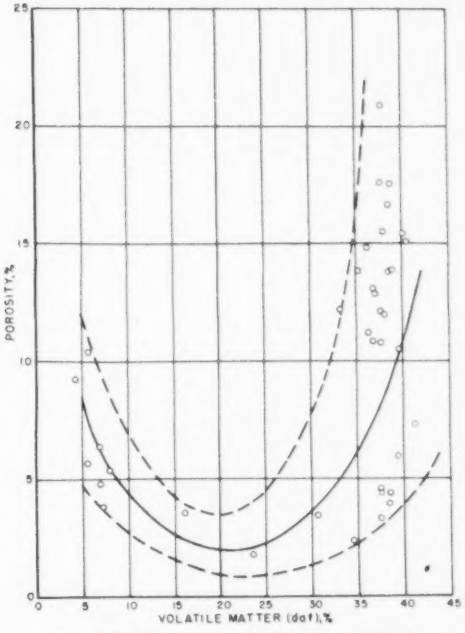

Fig. 4-S. Porosities of Coals of Differing Volatile Matter Contents[86]

positive swelling, that swelling increases with the rate of heating, and that bright coal swells more than dull.

On the basis of internal structure, the anomalous fluidity-expansion behaviors of coals at the limits of the coking band are accounted for, since these coals would not be expected to swell sufficiently to form continuous plastic layers.

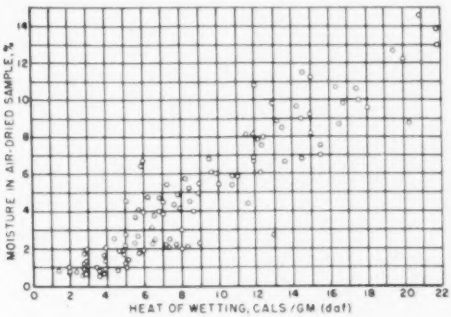

Fig. 5-S. The Relation Between Heat of Wetting and Air-Dried Moisture Content of Coals[77a]

III. Mechanism of Development of Expansion Pressure

According to H. Koppers, expansion pressure is due to the entrapment of gases of decomposition within the plastic layer, the pressure being dependent upon the viscosity of the layer and the rate of gas evolution.[89] After the pressure compresses the charge to its maximum bulk density, the full expansion pressure must be exerted on the oven walls. If only a slight coke shrinkage occurs, pressure on the walls is maintained as the plastic layer progresses toward the mid-plane of the oven. At the time of meeting of the plastic layers, nearly all expansion pressure curves show a peak.

Russell has assigned the cause of expansion pressure to the entrapment of gases within a continuous plastic envelope formed by plastic layers moving in from walls, floor, roof, and doors.[167] "Near the end of the coking period when the plastic seams are meeting at the center of the oven, and with the envelope still entrapping the gases, the rate of heating increases sharply . . . [due to predrying and preheating prior to gas evolution and to the effect of heating from both walls] . . . thus increasing the amount of gas evolved with the net result that the pressure rises rapidly." Representative expansion pressure curves are shown in Fig. 6-S.[167] It has been found that low- and medium-volatile coals ordinarily exhibit the peak pressure described, to the extent shown in Fig. 10-S. In the case of high-volatile coals, the envelope is comparatively permeable, and this, together with the large coke shrinkage, permits the easy escape of gas; consequently, in many cases no peak pressure results.

These explanations indicate that a number of simultaneous, separate processes are involved in the build-up of gas pressure within the plastic coal, and the net pressure is transmitted to the walls. The effects of each of these variables upon coal expansion will be separately considered.

A. Compressibility of Charge. The probable effect of this factor is the reduction of expansion pressure during the early part of the carbonization period. The pressures within the plastic layers during this period may be relieved by expansion of the layer and compression of the uncarbon-

ized coal between the layers. However, there is no possibility of pressure relief in this manner with charges of high bulk density, and after maximum bulk density has been attained with charges of low bulk density.[59] Although no experimental evidence is offered, coals of the same bulk density are considered to have similar compressibility characteristics.[185] Consequently, while this factor may partially explain the course of pressure during carbonization, it does not account for the wide differences which have been observed in the expansion behaviors of different coals.

B. Coke Shrinkage. Measurements by Auvil and co-workers of the shrinkages of cokes from various coals indicated that all shrank to practically the same extent, approximately 10.5 linear percent.[13] Other investigators found that the shrinkage varied from 9% for coke from low-volatile coal to 12% for coke from high-volatile coal.[185] This coke shrinkage throughout the carbonization period undoubtedly tends to relieve the gas pressures developed in the plastic layers and plastic envelope. However, comparative gas and wall pressure measurements, to be discussed later, show that the coke piece is pushed out to the wall during the expansion process, thus minimizing any possible effects of differences in coke shrinkage.

C. Existence of Plastic Layers and Plastic Envelope. Visual evidence of plastic envelope formation by advancing plastic layers has been provided by photographs of partly-coked experimental charges.[136, 165] Russell confirmed the presence of a plastic envelope by the indirect method of injecting nitrogen into the center of an expansion-oven charge.[167] Each injection was accompanied by an increase in wall pressure. Runs were also made where the top of the plastic envelope was kept open by a layer of coke breeze on top of the coal charge.[57, 165] The pre-peak expansion curve for this type of charge closely duplicated that for coal alone; the peak expansion pressure which had been observed with coal alone was eliminated by the breeze covering. These tests indicated that the peak pressure was due to gas pressure within the plastic envelope. (Since no reduction in pre-peak pressure was observed, the source of pre-peak pressure must be other than in the plastic envelope. Gas pressure measurements, to be discussed below, indicate that for coals with well-defined plastic properties the pre-peak pressure is due to gas pressure in the plastic layer itself).

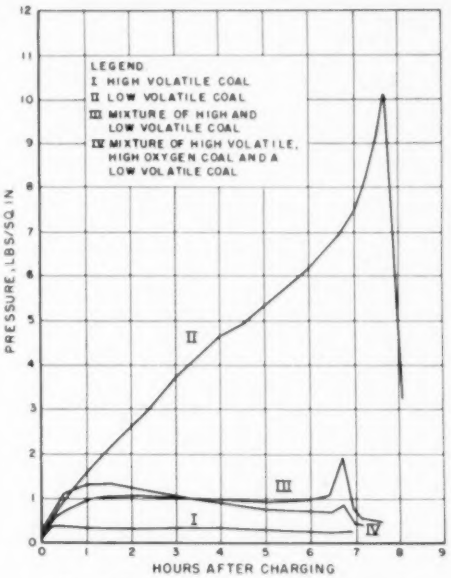

Fig. 6-S. Typical Russell Oven Expansion Pressure Curves[167]

Widening the top of the oven and reducing the top flue temperature also eliminated the peak expansion pressure by permitting the easy escape of gases from the interior of the charge.[165]

D. Gas Pressures within the Charge. The relationship between average wall pressure and the gas pressures measured at different distances from the wall is evident from the course of these pressures during the tests charted in Fig. 7-S.[144] The progression of the plastic layer past the sampling points is indicated by the successive increases and decreases of gas pressures in the tubes. During the pre-peak period, the wall pressure approximated the gas pressure at the sampling point which coincided with the position of the plastic layer. Since the gas pressures in the middle of the charge were low during this period, the gases formed on the cold side of the plastic layer must have been leaving the charge at an area of low resistance. The relative pressures indicated that the pre-peak wall pressures were due to gas pressures within the

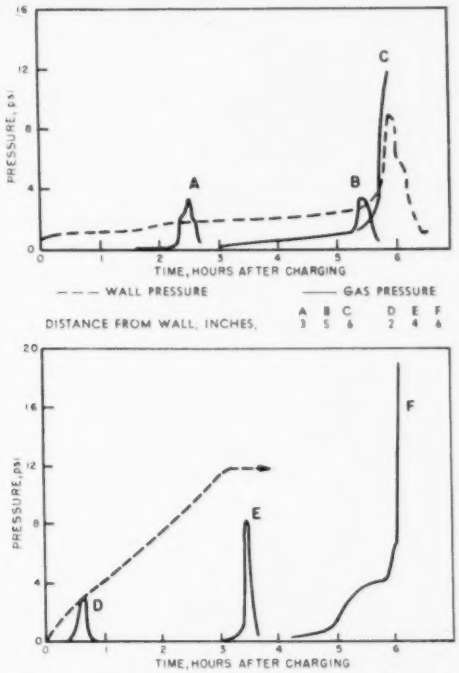

Fig. 7-S. Wall and Gas Pressures in Movable-Wall Test Oven[144]

individual plastic layers, and not from gas pressure within the plastic envelope. The expansion pressure of the plastic layer was transmitted on one side by the coke to the oven walls, and on the other side was neutralized by a similar force, from the opposite plastic layer, transmitted by the compressed coal particles.

The gas pressure in the middle of the charge gradually increased as the plastic layers approached each other in the mid-plane of the oven, and then rose to a sharp peak, coinciding with the occurrence of a peak wall pressure. The simultaneous occurrence of these peaks definitely established the source of the peak wall pressure. The peak gas pressure was ordinarily higher than the peak wall pressure; this difference may be accounted for by the following: 1) the mid-plane gas pressure was not effective over the entire wall area, because of coking from ends, top, and bottom; 2) the envelope was sufficiently rigid to contain a portion of the gas pressure.

The relationship between peak wall pressure and peak mid-plane gas pressure was more than qualitative. Naugle has expressed the results of 26 tests in the Bureau of Mines slot oven with 95% accuracy by the equation:[135]

$$\text{Gas Pressure} = 1.95\ \text{Wall Pressure} - 0.83$$

Gas pressures in the plastic layer and plastic envelope accounted for the expansion pressures of the coals of most practical interest, those having sufficient plasticity to exhibit peak pressures.

A different type of expansion must be operative for coals which exhibit a maximum pressure during the early part of the carbonization period. These coals included those at the limits of the coking band, oxidized coals, and high-inert charges. Low-rank and oxidized coals (Curve IV, Fig. 6-S) gave initial wall pressures of the order of 1.5 psi with little or no peak pressure, while semi-anthracite[144] coals gave initial pressures as high as 4 psi and no peak. Since fusion in these coals was poor, it is probable that there were discontinuities in the plastic layer or plastic envelope. For these coals, the wall pressure must have been due to gas pressure within the individual coal particles.

E. Thickness of Plastic Layer. Direct measurements of this dimension have been made in the laboratory with varying degrees of success, and partly-coked experimental charges[53] have given some information. However, most of the measurements have been made by indirect methods. Naugle estimated the thickness by plotting isotherms of Davis plasticity limits on a graph of temperature progression using coordinates of time and distance from wall.[134] Similar estimates were made by Russell from Gieseler plasticity and temperature progression data.[167] The thickness of the plastic layer was defined as the distance in the charge corresponding to the upper and lower temperature limits of plasticity, and was calculated:

$$\text{Thickness (in.)} = \frac{\text{plastic range (°C)}}{\text{temp. gradient in plastic layer (°C/in.)}}$$

Plotting of the data for a typical coal showed that during carbonization the thickness of the vertical plastic layers steadily increased from zero at the start to 0.5 in. at the sixth hour; at 6.7 hours the two layers met to form a double plastic layer 1.7 in. wide. Calculations on 25 coals showed that

the double layer may be as much as 3.9 in. thick at low rates of heating.

F. Path of Gases from Plastic Layer. The relative proportions of gases leaving the hot and cold sides of the plastic layer and the paths taken by these gases have been subjects of limited investigation. The gas pressure curves in Fig. 7-S indicate that the gases leaving the hot side of the plastic layer may pass through the coke with a negligible pressure drop, but the cold-side gases frequently build up considerable pressure when the plastic layers meet. There are various theories concerning the factors which influence the relative proportions of hot- and cold-side gases. Sapozhnikov concluded that the thickness of the plastic layer was determinative, since as much as 70% of the total gas was evolved on the cold side when the plastic range was narrow, and only 10% when the plastic layer was wide.[172] Soth and Russell suggested that the relative proportions may be estimated from the resistances on the hot and cold sides, resistance being defined as the temperature interval enclosing fluidities of less than 50 divs. per min. (cross-hatched area in Fig. 2-S).[185] The variations in hot- and cold-side resistances may partially account for the difference between the expansion behaviors of low- and high-volatile coals. Although the low-volatile coals evolve less total volatile matter, a greater volume may be evolved on the cold side than with high-volatile coals.

Smith concluded, from the sudden enrichment of the gas at the time of meeting of the plastic layers, that the cold-side gases leave the charge through the more permeable area at the top of the charge.[23] He reasoned that the hot-side gases are severely cracked to secondary products during their long passage through the hot coke and along the wall; the cold-side gases are cracked to a lesser extent, since the time of contact with hot coke is short during their passage through the shallow layer at the top. At the time of meeting of the plastic layers, the rate of evolution of the cold-side gases rapidly increases, leading to an apparent enrichment of the total gas. Another factor contributing to enrichment may be the final pyrolysis of oils and tars condensed from the cold-side gases in passing through the unheated coal.

Other evidence concerning the path of the cold-side gases is provided by tests where these gases were confined within the charge, the only avenue of escape being toward the heating wall through the vertical plastic layers.[71, 195] High pressures were generated, even with coals which were non-expanding under normal coking conditions. These experiments indicate that the internal gases normally escape from an area of lower resistance than the vertical plastic layers.

G. Theory of Mechanism of Development of Expansion Pressure. As coking coal passes through the range of carbonization temperature, the occurrence of the simultaneous processes of rapid volatilization and softening of the coal substance causes swelling of the particles. The force causing swelling is the pressure of the internal gases, which are partially constrained by the capillary structure of the coal.

For coals forming continuous plastic layers, the restraints imposed by walls, floor, and the weight of the superincumbent coal permit this internal pressure to deform the softened particles into a plastic layer, which entraps bubbles of gas. The pressures within these bubbles must rise to a value high enough to enable the passage of the gas from the plastic layer, resulting in a pre-peak pressure upon the oven wall. For low-volatile coals (Fig. 6-S, curve II), the gas pressures within the plastic layers increase as the layers progress toward the middle of the oven, possibly due to the thickening of the layers. At the time of meeting of the layers, the rate of temperature rise increases sharply, with a consequent increase in the rate of gas evolution. Since the area of escape for the gases within the plastic envelope is now greatly restricted, these factors cause a rapid increase in the mid-plane gas pressure, with an accompanying increase in wall pressure.

The higher-ranking high-volatile coals (Fig. 6-S, curve I) produce highly fluid plastic layers which at no time offer any substantial resistance to the flow of gas. Typical blends of low- and high-volatile coals (Fig. 6-S, curve III) produce plastic layers in which a pressure of about 1 psi is developed during the pre-peak period. The pressure rises to about 2 psi only under the exaggerated conditions (high rate of gas evolution due to drying and preheating the axial coal mass during the earlier carbonization period and to the accelerated temperature rise from the effect of heating from two sides) present at the time of meeting of the plastic layers.

The coals which form non-continuous plastic layers (coals at the limits of the coking band, oxidized and high-inert charges, and their mixtures) develop maximum pressure during the early part of the coking period, and little or no peak pressure (Fig. 6-S, curve IV). Since these coals are characterized by low fluidity, poor swelling ability, and poor fusion, it is not probable that carbonization pressure results from gas pressures within either the plastic layer or plastic envelope. The comparatively open physical structure of these coals permits only slight swelling. The usual result is low wall pressures, whose source is gas pressure within the coal particles themselves.

IV. Present Practice in Expansion Testing

For expansion testing purposes, two types of measurement are made. At most test installations in this country, expansion pressure is measured in a two-wall-heated oven, usually of the Russell type, with one wall movable. A smaller number of sole-heated ovens of the Brown type are used to determine volume expansion and shrinkage. In a few plants, both types of testers are used. Laboratory testers and mechanical devices for expansion measurements within full-scale ovens are not generally used in this country, since it has been found that they provide either incomplete or unreliable information. A comparison of the procedures used at various plants for controlling expansion indicated a variety of testing methods, and no consistent interpretation of results. Analyses of the practices at these individual plants revealed wide variations in bulk densities and rates of carbonization, which could account for the different expansion criteria used.

V. Influence of Variable Carbonizing Conditions upon Expansion

The effect of various factors upon expansion was ascertained from a study of published data obtained principally with the two main types of expansion testing equipment mentioned above.

A. Bulk Density. The relationship between dry coal bulk density and log of maximum expansion pressure may be approximated by a straight line of slope 0.10 (Fig. 8-S). The effect of bulk density

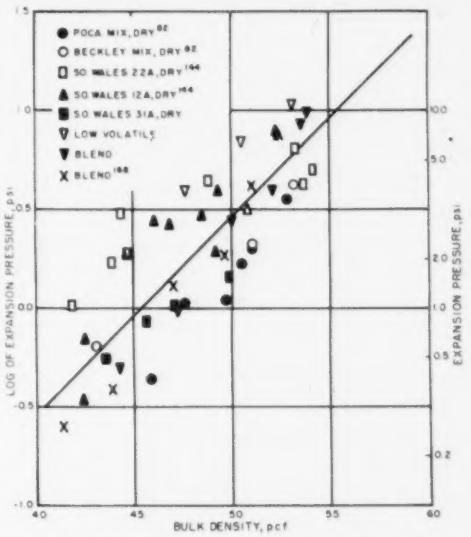

Fig. 8-S. Effect of Bulk Density on Expansion Pressure in Russell Oven

upon volume expansion may be accurately represented by the following equation:[12]

$$E_x = \left[\frac{W_x}{W_f}\left(100 + E_f\right)\right] - 100$$

E_x = volume expansion at W_x bulk density, %
E_f = volume expansion at W_f bulk density, %
W_x = standard bulk density, pcf
W_f = test bulk density, pcf

Since bulk density exerts such a significant influence upon expansion behavior, consideration should be given to some of the factors which influence bulk density. Size distribution was found to be the dominant factor governing the bulk density of air-dried coal in the ordinary range of sizes charged to ovens, the highest bulk densities being obtained with the widest distribution of sizes.[33] The particle size was found to govern the minimum bulk densities of coals to which water had been added (Fig. 9-S). This behavior suggested that the surface area was the significant factor for wet coals. Calculation of the relative surface areas showed that the minimum bulk densities were reached at a moisture content of approximately 0.13% moisture per unit surface factor. The addition of small amounts of oil has been found to be

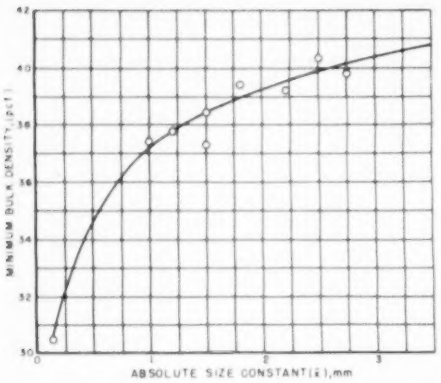

Fig. 9-S. Effect of Particle Size on Minimum Bulk Density of Wet Coal[33]

due to moisture fluctuations.[94, 150] Of numerous other factors which affect bulk density, attention should be called to the large increases in bulk density caused by freezing of the surface moisture on the coal particles.[5]

The bulk densities throughout an oven are not uniform, because of the effects of dropping the charge and levelling.[55] The regions of maximum bulk density correspond with the regions of initial wall failure.

B. Particle Size. The main effect of particle size is upon bulk density; at constant bulk density, finer pulverization may lead to slight increases in expansion pressure.[52] The volume expansions (dry, solid coal) of 31 coals were increased an average of 2%, for each 10% increase in the percentage of minus 4-mesh coal.[151]

C. Rate of Heating. In general, faster rates of heating increased expansion pressure and volume expansion, with some indication of the pressure reaching a maximum at flue temperatures of about 2300 F. From a theoretical standpoint, faster rates of heating should increase the rate of gas evolution, which would tend to increase the expansion pressure; at the same time, the thickness of the plastic layer would be decreased, and the fluidity increased, both of which would tend to decrease the expansion pressure.

D. Oven Width. The expansion pressures of the more highly-expanding coals decreased as the oven width was increased from 6 up to 10 or effective in reducing the bulk density variations 12 inches. For widths greater than 12 inches, no consistent effect of oven width upon the expansion pressures of different coals could be noted. The explanation for this non-consistent effect is probably to be found in the relationship between rate of heating, discussed above, and oven width (the coking time has been found to vary approximately with the 1.8 power of the oven width[102]). At the time of meeting of the plastic layers, the increased resistance to heat flow through the longer coke pieces in wider ovens would undoubtedly decrease the effective rate of heat transfer to the middle of the charge. From the remarks made in **C. Rate of Heating**, this lowered rate of heating may either decrease or increase the pressure, depending on the relative influences of the other factors.

E. Heating Conditions. Comparative expansion pressure tests[105, 102] with one wall and two opposite walls heated show that the two methods of heating gave substantially identical expansion pressures during the pre-peak period; one-wall heating failed to give the pressure peak observed with two-wall heating, since the conditions necessary for the development of peak pressure are not present when heating is from one wall only.

Almost all comparative data for the two methods of heating are in the form of expansion pressure at constant volume in two-wall heated ovens, and volume expansion or contraction at constant pressure (2.2 psi) in sole-heated ovens. Attempts to correlate the results of these two methods of test over the complete range of coking coals have proved disappointing. However, for the coals showing both expansion pressures in the higher ranges and positive volume expansions, there appears to be a possibility of relationship. This would imply a relationship between expansion pressure and volume expansion for one-wall heating, and a relationship between pre-peak and peak expansion pressures for two-wall heating.

F. Relative Size and Shape of Testing Equipment. Measurements of expansion pressures in a small-scale (17 lb. charge) two-wall heated coke oven have given higher results than those obtained with larger-scale apparatus, but sufficient reproducibility could not be obtained for correlation of the results.[134] The reasons given for lack of reproducibility were rupture of the plastic envelope at varying pressures during free-top tests, and variable cooling during confined, cooled-top tests.

VI. Influence of Coal Properties upon Expansion

A. Chemical Composition.

1. Indications of Rank. The following indications of rank have been used by various investigators for correlation of expansion behavior:

Volatile Matter, daf vs. Volume Expansion[34]

Volatile Matter, daf / Carbon, daf vs. Expansion Pressure[141]

Volatile Matter, dmmf plus Moisture vs. Expansion Pressure[141]

The present study of Bureau of Mines data on expansion pressure and volume expansion showed that the correlations with volatile matter could be improved if the volatile matter values were corrected for CO_2, and the expansions were corrected to a standard bulk density at uniform mineral matter. The latter term approximates a standard volume of solids per unit volume of charge, rather than a standard bulk density, thus correcting for the effect of mineral matter upon bulk density. The volume expansion data (Fig. 11-S) indicate that a maximum is reached at 17% volatile matter content, with a lesser peak at 27%. Because of the almost vertical rise of the curves, the relationship is not useful below 18% volatile matter. Above 31% volatile matter, the correlation was poor.

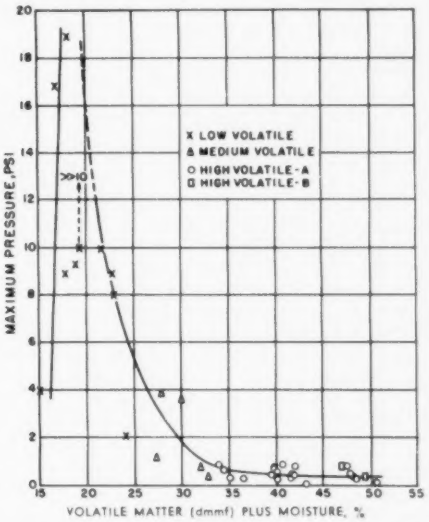

Fig. 10-S. Expansion Pressures of Unblended Coals in Russell Oven[141]

2. Ash or Mineral Matter Content. Although some test data have indicated that expansion is significantly affected by mineral matter content,[35, 82] it is probable that the major effect of mineral matter is upon bulk density, with only a slight independent influence upon expansion. The lower part of Fig. 11-S shows the almost negligible effect of mineral matter in reducing expansion, when results were corrected to a standard bulk density at uniform mineral matter.

The rather large corrections for mineral matter found necessary when correlating with fluidity (Fig. 12-S) were probably due mostly to the effect of mineral matter upon fluidity.

3. Degree of Oxidation. The limited data available indicate that expansion pressures were reduced by the use of oxidized charges or the addition of oxidized coals to an otherwise normal blend.

The volume expansions of nearly all expanding coals were decreased by oxidation,[45] although one coal showed an increase with moderate oxidation.[52a] The contraction of a contracting coal was decreased by oxidation.[46]

These effects of oxidation upon expansion may be reconciled by consideration of the effects of oxygen upon the coal. The decreased fluidity[107] accompanying oxidation may be explained upon the basis of alteration of the chemical structure by removal of hydrogen and addition of oxygen; if the plastic layer is continuous, the decreased fluidity would tend to increase expansion. The well-known effect of oxidation in the reduction of swelling, as measured by the swelling index and a volatile matter button, should also be considered. Recent evidence indicates that this decrease in swelling is due to the opening of the capillary structure by oxidation.[19] Decreased swelling would of course lead to increased permeability of the plastic envelope and consequently to a lower expansion pressure.

B. Physical Tests

1. Fluidity. The relationship between Gieseler maximum fluidity and expansion pressure has been shown in Fig. 1-S.

A comparable plot of fluidity and volume expansion, as measured in the Bureau of Mines sole-

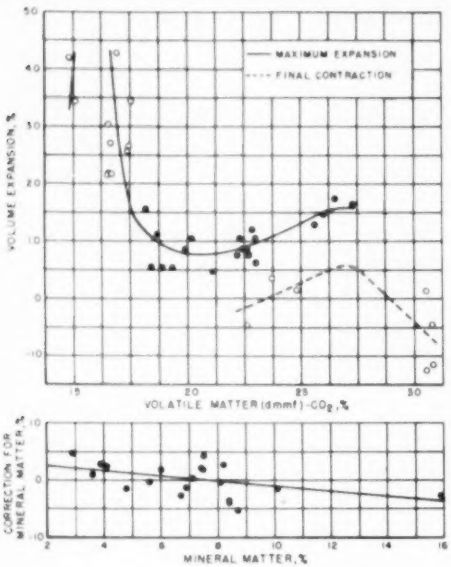

Fig. 11-S. Volume Expansion as a Multiple Function of Volatile Matter and Mineral Matter

Note: Test expansions have been calculated to expansion at a standard dry bulk density of 54 pcf at 8% mineral matter. Expansions in the upper graph were corrected to 8% mineral matter by the average line shown in lower graph. Data from Table III, pp. 43-44.

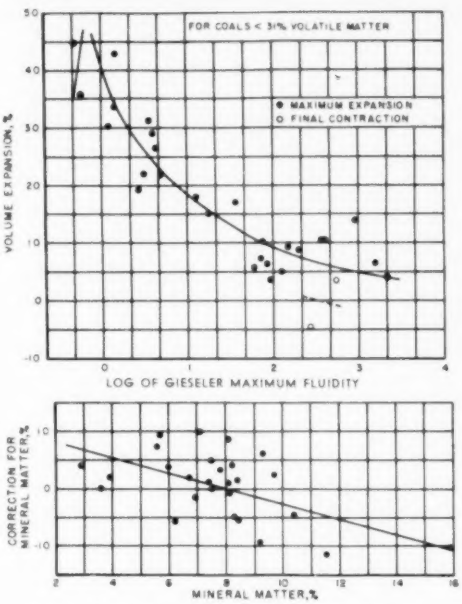

Fig. 12-S. Volume Expansion as a Multiple Function of Fluidity and Mineral Matter

Note: Test expansions have been calculated to expansion at a standard dry bulk density of 54 pcf at 8% mineral matter. Expansions in the upper graph were corrected to 8% mineral matter by the average line shown in lower graph. Data from Table III, pp. 43-44.

heated oven, is shown in Fig. 12-S. It has been mentioned that the large correction for mineral matter is probably due to the effect of mineral matter upon fluidity. This would indicate that the significant factor is the fluidity of the coal substance itself rather than of the mixture of coal and mineral matter. No relationship between fluidity and volume expansion was apparent for coals of more than 31% volatile matter. The similarity of this volume expansion curve to that shown for expansion pressure (Fig. 10-S) is a strong indication that a relationship exists between these two properties in the range of perhaps 14 to 31% volatile matter.

2. **Other Plasticity and Swelling Tests.** Among other plasticity and swelling tests, the free swelling index,[17,58] agglutinating index,[92] and laboratory swelling tests[105] should be mentioned. Although it has not been possible to apply these tests directly to coal expansion, some of them have been found useful in studies of low-rank coals[139a] and in the detection of oxidized coals.[176, 206]

3. **Differences in Ultra-Fine Structure.** Available data on the effect of differences in ultra-fine structure upon the expansion behavior of coals are limited to what may be inferred from total and air-dry moisture contents. From the data given in **Swelling vs. Internal Structure,** p. 21, these measures furnish some indication of relative porosities and surface areas.

The relationship of air-dry moisture to expansion behavior was determined from Bureau of Mines data on volume expansion. The air-dry moisture was found to be of little significance for the expanding coals, since all coals which expanded more than 1% contained substantially the same amount of air-dry moisture, 0.65 ± 0.25%. For the coals of more than 31% volatile matter (mostly contracting), the air-dry moisture was found to be significant in multiple correlation with volatile matter (Fig. 13-S). Volume expansions in this range of volatile matter could not be successfully correlated with volatile matter or fluidity, alone or in combination.

Comparable expansion pressure data for un-

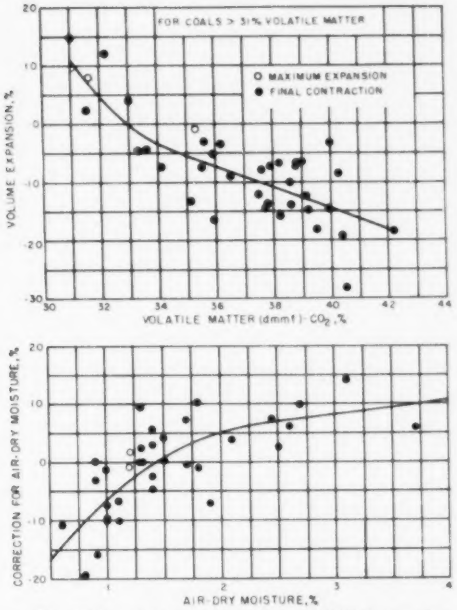
FOR COALS > 31% VOLATILE MATTER
O MAXIMUM EXPANSION
● FINAL CONTRACTION
VOLUME EXPANSION, %
VOLATILE MATTER (dmmf): CO_2, %
CORRECTION FOR AIR-DRY MOISTURE, %
AIR-DRY MOISTURE, %

Fig. 13-S. . Volume Expansion as a Multiple Function of Volatile Matter and Air-Dry Moisture

Note: Test expansions have been calculated to expansion at a standard dry bulk density of 54 pcf at 8% mineral matter. Expansions in the upper graph were corrected to 8% mineral matter by the average line shown in lower graph. Data from Table III, pp. 43-44.

blended coals are not available, but in the section on the expansion of coal blends **(Coal Mixtures,** p. 51) it will be shown that the air-dry moisture of the high-volatile coal was the most significant variable which could be identified.

4. Petrographic Composition. Hand-picked bright fractions showed greater expansion pressures and volume expansions in laboratory expansion tests than the corresponding dull fractions.[123, 199] There is some evidence that the differences in the expansion behavior of the petrographic constituents may be explained on the basis of differences in internal structure, since vitrain apparently has smaller capillaries than durain or fusain.[86] While the effect of petrographic composition is evident in picked fractions, with full-seam samples of American coals it was not found possible to correlate expansion behavior with petrographic composition, probably because of the narrow range of composition of these samples.

The addition of inerts, such as anthracite fines, low temperature coke and coke breeze, decreased

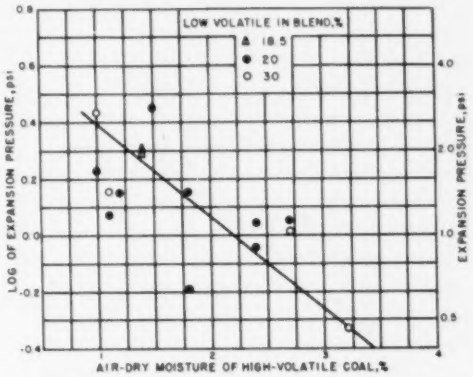

Fig. 14-S. Expansion Pressures of Coal Blends vs. Air-Dry Moistures of the High Volatile Coal

Note: Test pressures have been converted to pressures at a standard dry bulk density of 49 pcf at 8% mineral matter (see Fig. 31, p. 46.) Data from Table X, p. 54.

expansion pressures.[168] These materials probably increase the permeability of the plastic layers.

C. Coal Mixtures. The volume expansion of blends of high- and low-volatile coals may be calculated within an average error of 1.7% from the following equations:

20% Low-Volatile Blend: $E_B = 0.728\ E_{HV} + 6.4$

30% Low-Volatile Blend: $E_B = 0.576\ E_{HV} + 7.1$

E = expansion at wet bulk density of 55.5 pcf, %

B and HV refer to blend and high-volatile, respectively.

The volume expansion of a blend in this range of composition is therefore primarily a function of the expansion of the high-volatile coal. (It has been shown that the expansion of a high-volatile coal is related to the volatile matter and air-dry moisture.)

The expansion pressures of blends of high- and low volatile coals deviate widely from the weighted average of the pressures of the constituent coals. While the data on blends are far from complete, it was found that the expansion pressures of 15 blends, containing from 17.5 to 30% low-volatile coal, were more closely related to the air-dry moisture of the high-volatile coal than to any other factor (Fig. 14-S).

Although Russell[168] has shown that the expansion pressures of some binary blends varied inversely with the blend fluidities, other investigators[82] found that expansion may be decreased by substitution of coals of either high or low fluidity for one of moderate fluidity.

APPENDIX

I. Damage To Oven Walls

Coke oven walls are subject to severe service conditions in that they must resist load, abrasion, the chemical action of gases, and thermal shock. The recognized causes of premature failure of coke oven walls include:[78, 84]

Distortion and destruction by the expansion pressure of the charge.

Disruptive forces exerted by the pusher when there has been insufficient final contraction of the charge. The pressure transmitted to the oven walls when attempting to push a sticker has been calculated from the observed amperage to be as high as 6 psi.[62]

Abrasion and thermal shock encountered when excessively wet coal is dropped into the oven chamber.

Too-rapid heating or cooling schedules, particularly in the case of used brick.

Slag attack due to the combination of high temperatures and fusible coal ash, such attack being especially serious with dry coals.

Excessive cooling of oven ends when doors are off for long periods.

This report is concerned with the prevention of damage due to coal expansion, including both the expansion pressure and volume expansion of the charge. The type of wall damage which is ascribed to the use of expanding coals has been most completely described by Kerr and Taylor.[84] It is characterized by spalling, usually one-quarter to two inches deep, at the face of the bonder (header) brick and the adjacent edges of the stretchers. The spalling occurs initially across the walls in the lower courses, then extends up the walls, particularly near the ends. The fracturing of the bricks then proceeds across the wall in a band slightly below the top of the charge. (From this description it may be seen that the damage originates in the regions of highest bulk density, and also in the areas which bear the maximum transmitted pressures of the pusher ram.) Inspection of several batteries showed that the damage does not occur on the end-oven outer wall, which is backed up by the pinion wall, but usually starts on the opposite wall and gradually extends across the battery. If the damage is noted before the walls are seriously bowed, patching may sometimes be successfully applied. However, if serious damage has occurred, the walls must be torn down and rebuilt.

Koppers Company is quoted as stating that the first noticeable effect of damage by expanding coals is spalling of the liner brick at the coal line about two flues in from each end of the oven.[82] The spalling spreads in a "V" down the walls toward the center of the oven about two courses above the oven floor. If this spalling is allowed to continue, the ends of the bottle brick break off and the wall becomes distorted. The wall may develop holes and fail completely.

The expansion pressures which may be exerted are obviously of great magnitude, although they have never been precisely measured. Some idea of the forces which may be generated can be gained from a test reported by Barritt,[16] in which an end-oven was used for experimental purposes. The adjacent oven was filled with firebrick in courses, giving a total masonry thickness of $63\frac{1}{2}$ in. A 10 ft. charge of expanding coal in the end-oven displaced the two oven walls and firebrick filler a distance of $1\frac{3}{4}$ in. Obviously, forces of this magnitude cannot be contained by a structure of any reasonable dimensions.

Although the absolute strength of coke oven walls under actual conditions of operation is not known, the experiments of Koppers and Jenkner may be cited.[59] They found that initial cracks were formed in a model wall at 1.3 psi. At higher pressures, the rate of deformation increased rapidly. It is of interest to note that the pressure at initial cracking is approximately equal to the criterion for dangerous coals arrived at by analysis of test-oven expansion data (Appendix IV, C, p. 33)

II. Mechanism of Carbonization

In an effort to explain the process of carbonization, many references have been made to the existence of a chemical coking constituent or coking principle in coals. According to Fisher, coal is composed of oil-bitumen, responsible for coking ability, and solid bitumen, responsible for expanding ability.[123] The solvation theory of Agde and Hubertus attributes swelling to the absorption of liberated bitumen by the solid residue.[26] In Wheeler's "rational analysis" of coal, the coking constituent was identified with a particular coal fraction isolated by fractional extraction.[29] Remixing of the extract with the residue has led to conflicting conclusions as to the coking properties of the reconstituted

coal. While these and similar theories explain certain aspects of carbonization, none has won general acceptance.

Considerable success has been achieved in describing carbonization as a physical process. Mott has demonstrated that the coking coals are characterized by swelling of individual particles, and that a certain degree of swelling is necessary to fill the voids in a particulate charge.[127, 129] Macura, from motion pictures of laboratory coking, concluded that the process consisted essentially of fusion or sintering of the swollen particles, and that a homogeneous melt was not formed at ordinary rates of heating.[111] Complete fusion of the coal appears to be ruled out also by recent research showing that the physical structures of chars produced at different temperatures were determined by the physical structures of the coals used.[65, 120]

Softening of the coal substance is implied by the swelling and fusion of coal particles when heated, even if direct evidence for softening did not exist. However, fluidity measurements have shown that the coking coals soften when heated to carbonization temperature.[111-3, 167]

The processes of swelling and softening are accompanied by devolatilization. Another factor to be considered is that pressure is necessary for the formation of a well-fused coke.[167] In the ordinary coking process, the pressure results from the weight of the superincumbent coal and the pressure of the gas entrapped in the coal particles, plastic layer and plastic envelope. This pressure must be sufficient for deformation of the softened, swollen particles into a coherent mass, but must be restricted to avoid damage to oven walls.

The process of carbonization of particulate coal may therefore be described from the physical standpoint as one in which the influence of heat causes the particles to soften, swell, and devolatilize, sufficient pressure being present to compress the swollen particles into a coherent mass. These processes will be described separately in the following sections, although it is recognized that they occur simultaneously.

A. Softening

There appears to be no difference between the softening of coal under the influence of heat and the usual melting of a solid. To quote Berkowitz:[19] "Due to the increased thermal oscillations of molecules or atomic groups at the micellar surface, a rapid diminution of the intrinsic strength of the coal is to be expected."

The most widely-used instrument for measurement of the change with temperature in the fluidity of the pulverized coal mass has proved to be the Gieseler plastometer, the Davis instrument being used less frequently. Four temperature-plasticity points are noted:[10]

1) Initial softening temperature
2) Fusion temperature (5 dial divs. min., rising)
3) Temperature of maximum fluidity
4) Solidification temperature

Typical temperature limits of plasticity have been given as follows:[167]

Typical Coal		Plastic Temperature Range, °C		
Rank	Volatile Matter %	Initial Fusion	Maximum Fluidity	Solidification
Low-Volatile	17	440	480	500
Med.-Volatile	22	395	475	505
High-Volatile	34	370	450	480
High-Volatile	38	380	440	465

Lowry and Junge have correlated the characteristic temperatures of plasticity with fixed carbon content.[103]

Various indices have been used to express the relative fluidities of coals, utilizing the results of Gieseler or similar tests. Macura introduced the concept of "total fluid power", and advocated the expression of the entire softening-process in rhe-second units.[111-118] McCartney and Davis' investigations of the relationship between fluidity and volume expansion indicated that the most useful abscissae were: 1) the mean resistance developed in the Davis plastometer; 2) the Gieseler mean fluidity; and 3) the area under the Gieseler temperature-fluidity curve.[108]

More recently, preference has been given to the use of the simpler term "maximum fluidity," expressed in dial divisions per minute. The relationship between maximum fluidity and rank has been shown by Russell and Perch (Fig. 1). Low-volatile coals ranged from 0 to 100 units, medium-volatile from 100 to 10,000, high-volatile A generally around 10,000 and dropping to as low as 2 in some cases, and high-volatile B from 20 down to 0. Calibration of the instrument with pitches of known viscosities permitted the conversion of dial speeds to absolute units.[184] The apparent maximum viscosities of low-volatile coals were found to be of the order of 10^5 poises, medium-volatile 10^4, high-volatile as low as 10^3, and high-volatile B as high as 10^6 poises. For purposes of

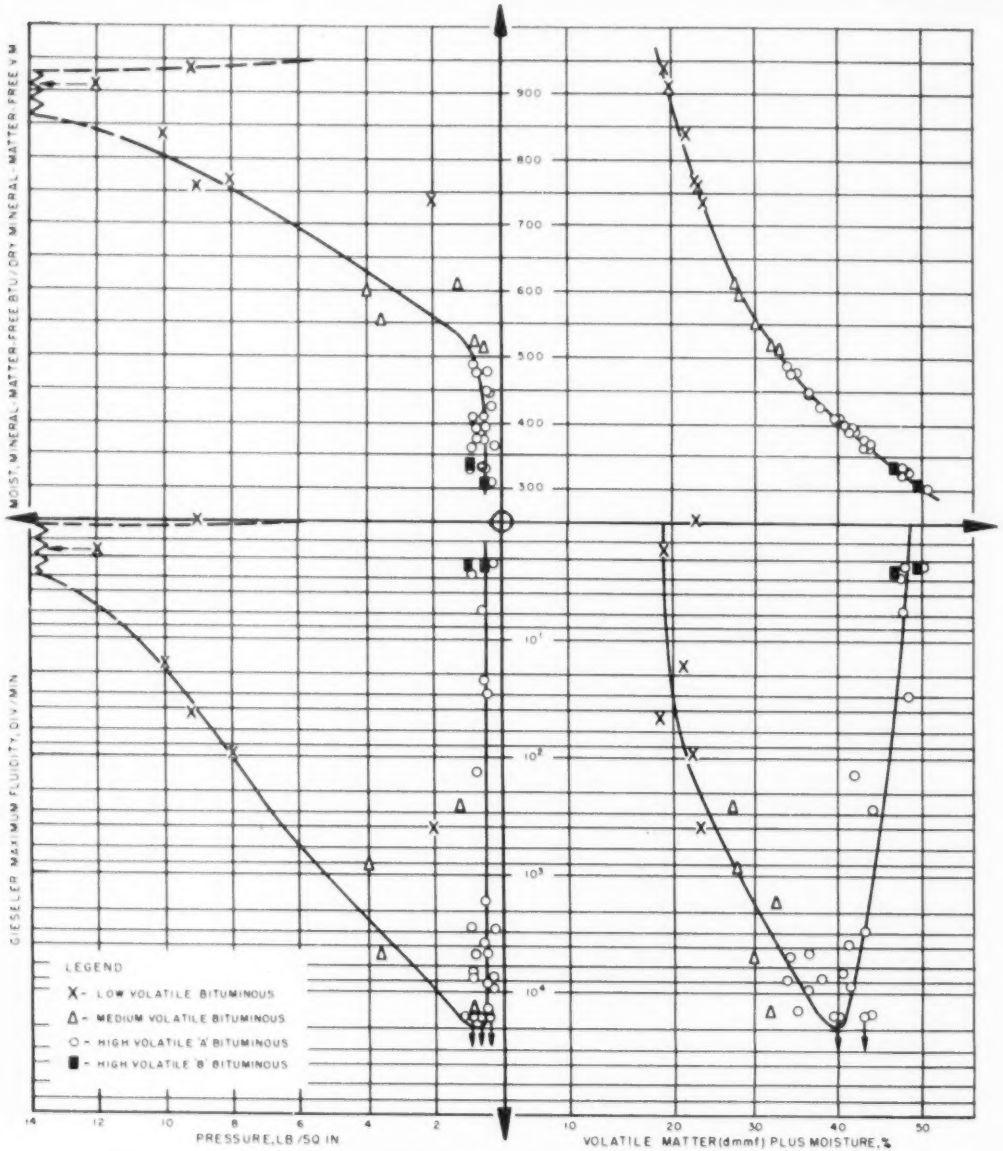

Fig. 1—INTER-RELATIONSHIPS OF EXPANSION PRESSURE, COAL RANK, AND GIESELER FLUIDITY

(Data from Russell and Perch)[167]

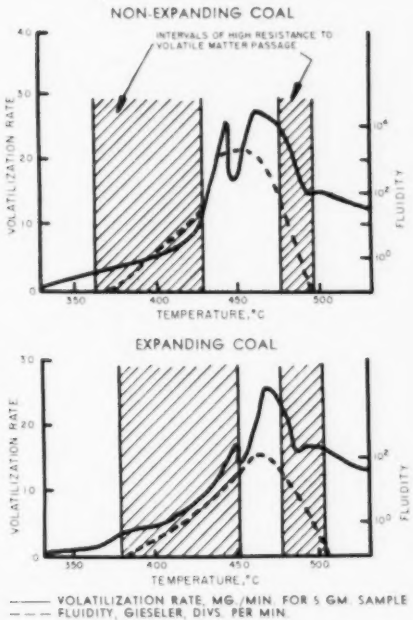

Fig. 2.—Fluidity-Volatilization Relationships[185]

comparison, it may be noted that molasses has a viscosity of about 10^3 poises, and confectioner's glucose about 10^4 poises.[142]

The influence of factors other than rank is also reflected in the fluidity behavior. Decreasing the heating rate shortens the temperature range of fluidity and decreases the fluidity itself.[113, 167] Oxidation of the coal has a similar effect.[167] Petrographic factors which tend to increase the fluidity of a coal above that expected from its rank include high concentrations of anthraxylon, translucent attritus, and the presence of cannel coal. Factors that tend to reduce the fluidity include high concentrations of ash, opaque attritus, and fusain.[30]

An inverse relationship between maximum fluidity and maximum expansion pressure would be expected. The complex relationship which actually exists has been shown by Russell and Perch (Fig. 1). Most of the low- and medium-volatile, and the higher-ranking high volatile coals show the expected inverse relationship. The lower-ranking high-volatile coals show both low fluidity and low expansion pressure. This anomaly is explained by the authors as being due to the greater shrinkages of the solidifying cokes from these low-rank coals, the shrinkages being sufficient to relieve any pressures developed within the viscous plastic layers.

Further applications of fluidity data to expansion behavior are considered in the following section and Appendix VI, B.

B. Rate of Volatilization

The change with rising temperature in rate of volatilization has been measured by several investigators,[111, 144] typical results being shown in Fig. 2. The inclusion of Gieseler fluidities on the rate-of-volatilization graph showed that the regions of maximum rates of gas evolution corresponded with those of maximum fluidity. Comparison of these graphs with the expansion pressure curves of the coals indicated that expansion pressure was due to the liberation of relatively large amounts of volatile matter during the time that the plastic coal was relatively viscous. The regions of high resistance were assumed to be the temperature intervals corresponding to fluidities of less than 50 divs. per min. These relationships were used to explain the development of expansion pressure with different kinds of charges, and to make qualitative predictions of expansion pressure. However, English investigators[144] were unable to discern any general dependence of expansion pressure upon the rate of volatilization and fluidity.

C. Swelling vs. Internal Structure

The mechanism of swelling can best be explained by consideration of the physical structure of coals. According to recent experimental work conducted in England,[95] coal consists of aggregates of molecules (micelles) separated by capillaries of average diameter approximating 40A. Measurements have been made of the capillary area and volume; from them the average diameter was calculated, and estimates made of the minimum diameter.

The extent of the capillary surface for a number of coals has been calculated from low-temperature adsorption isotherms, but relatively few data are available. More complete data are furnished by determinations of heats of wetting, which has been shown to be a relative indication of surface area (1 cal. equals approximately 10 m^2).[119] The heats of wetting with methanol for a large number of coals of particle size less

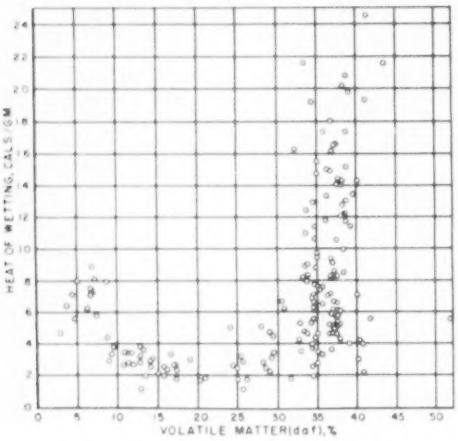

Fig. 3.—The Heats of Wetting of Coals of Differing Volatile Matter Contents[77a]

than 72-mesh Brit. Std. Sieve are shown in Fig. 3. More recent results for coals of -240 BSS indicate that the minimum heat of wetting should be raised from the value of about 2 shown in the figure, to 5, because of incomplete penetration by the methanol into the coarser sizes of the less porous coals.[47] With this qualification, the figure represents the relative surface areas of coals of differing volatile-matter contents.

The volume of the capillary spaces is represented by the porosity, which may be calculated from measurement of the "true" and apparent specific gravities. Plotting of calculated porosities against volatile matter (Fig. 4) showed the same type of curvature as was noted for surface area (Fig. 3). Comparison of these data indicated an approximate conversion factor of 1% porosity per 10 m^2 g of surface.

Since coals in the natural condition contain capillary moisture, relationships between moisture content and characteristics of the physical structure would be expected. Plots of total (bed) moisture vs. volatile matter,[141] and moisture at 50% humidity vs. volatile matter,[136] showed the same type of curvature as was noted for surface area and porosity. Air-dry moisture would probably show the same type of curvature, since it is related to total moisture (Fig. 33, p. 50). More direct evidence is found in the relationship between moisture content of air-dried coals and heat of wetting shown in Fig. 5.

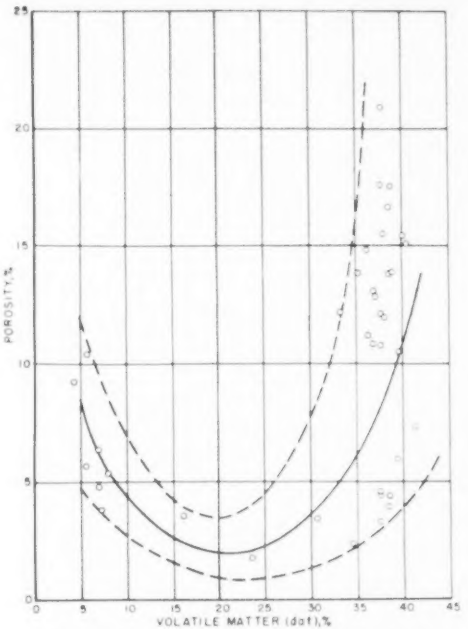

Fig. 4.—Porosities of Coals of Differing Volatile Matter Contents[86]

Further research on the physical structure by measurement of apparent densities,[64, 65] and heats of wetting[77, 120] of coals and chars, indicated "drifts" of density with time and variations in heats of wetting which could best be ascribed to differences in the molecular volumes of the liquids and gases used. Since the differences were too large

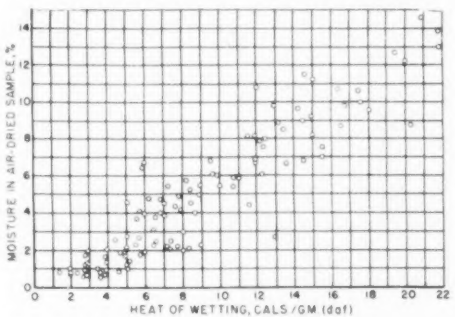

Fig. 5—The Relation Between Heat of Wetting and Air-Dried Moisture Content of Coals[77a]

TABLE I

SUMMARY OF RESULTS OF SWELLING OF 1-INCH CUBES[127]

Rate of Heating			1° Per Min	5° Per Min.
	% C, daf	%H, daf	Per Cent Swelling	
Bright Coal	90-87	4.85	34	134
	90-87	4.85-5.0	70	350
	89-88	4.85-5.0	70	350
	88-87		355	666
	86-85		160	325
	85-84		150	277
	84-83		90	120
	83-82		86	145
	82-81		37	55
	81-80		35	140
	80-79		22	70
	76		-16	12
Dull Coal	84		21	45
	84		-3	-8

to be explained by the average capillary diameter, it was postulated that the pore space contains numerous fine constrictions. The diameter at these constrictions would be of the same order as the molecular diameters of the gases and liquids used (2 to 5 angstroms). It was observed that drifts in density, and difficultly accessible pores, occurred most often with the coking coals.

The poorly-coking and non-coking coals are therefore characterized by a comparatively open type of capillary structure, whether judged by surface area, porosity, or constrictions. Studies of the internal structures of coals and their cokes produced at different temperatures showed that capillarity persisted throughout carbonization and therefore complete fusion of the coal did not take place.[95, 129] The accessibility of the inner surfaces to liquids and gases, however, was diminished with rising carbonization temperature.[27]

According to the theory of Berkowitz, the swelling of coal is due to gases formed by pyrolytic decomposition within the capillary structure described.[19] The rate of diffusion of these gases to the exterior of the particle will be governed by the pore diameter and constrictions. Since coking coals are of comparatively dense structure, a gas pressure will be built up within the pores. Because of softening of the coal substance, a stage will be reached when the yield stress of a particle has been reduced to a value below that of the internal pressure, and the coal distends. Since swelling does not necessarily produce a material of large internal surface, it is probable that the gases do not escape uniformly through all pore exits, but instead follow the paths of least resistance through the bigger pores and cracks. In confirmation of this theory, it has been found that slow rates of heating (0.5° C per min.) will greatly suppress swelling, and rapid rates will produce coke-like residues from normally non-coking coals.

The actual swelling of coal particles, both bright and dull, has been measured by Mott (Table I). The swelling was most pronounced in the direction perpendicular to the bedding plane of the coal. From these data, it may be concluded that:

1) The coking coals are characterized by high percentages of positive swelling.

2) Swelling increases with the rate of heating.

3) Bright coal swells more than dull coal.

Swelling of columns of coal particles (the Sheffield Coking Test) generally showed the same gradation with variations in carbon content as was found for single particles.

The anomalous fluidity-expansion behavior of coals at the limits of the coking band may be explained on the basis that the swelling of these coals is insufficient for the formation of continuous plastic layers. The reason for this lack of swelling may be found in the comparatively open physical structure of these coals. Physical structure is also useful in explaining the swelling behaviors of oxidized coals and petrographic constituents. For oxidized coals, both heat of wetting and porosity measurements indicate that oxidation leads to a more open type of structure.[19] Of the petrographic constituents, vitrain apparently has smaller capillaries than durain or fusain, since small hysteresis loops were observed for this constituent during moisture sorption.[86]

III. Mechanism of Development of Expansion Pressure

The basic theory of the mechanism by which expansion pressure is developed was proposed by H. Koppers, after close observation of the phenomenon on an industrial scale, and experiments with laboratory and movable-wall testers.[89] The origin of expansion pressure was ascribed to the entrapment of gases of decomposition within the plastic layer, the pressure being dependent upon the viscosity of the layer and the rate of gas evolution. After the pressure has compressed the charge to its maximum bulk density, the full expansion pressure must be exerted on the oven walls. If only a slight coke shrinkage occurs, pres-

sure on the walls will be maintained as the plastic layer progresses toward the mid-plane of the oven. At the time of meeting of the plastic layers, which takes place when the mid-plane temperature is about 500° C, nearly all expansion pressure curves showed a peak pressure.

The modern theory of the development of expansion pressure has been presented by Russell:[167]

> "In a coke oven, two plastic seams parallel to the oven walls are established soon after the coal is charged and progress toward the center of the oven. Because there is considerable heat in the roof, floors and doors, plastic seams are also started from these surfaces and progress away from them at a rate proportional to the heat available. In other words, there is a continuous plastic envelope around the uncarbonized coal from a time shortly after the coal is charged into the oven until the two plastic seams starting from the oven walls meet at the center of the oven. Gases evolved into the raw coal side of the plastic seams are therefore entrapped within the plastic envelope. Near the end of the coking period when the plastic seams are meeting at the center of the oven, and with the envelope still entrapping the gases, the rate of heating increases sharply (due to the effect from both walls) thus increasing the amount of gas evolved with the net result that the pressure rises rapidly. This is true with the low-volatile and medium-volatile coals that attain low and moderate fluidities respectively, but with high-volatile coals that become highly fluid the envelope, in consequence, is very permeable and this together with the large coke shrinkage results in easy escape of the gases and in many cases no pressure peak near the end of the coking period."

Typical expansion pressure curves are shown in Fig. 6.

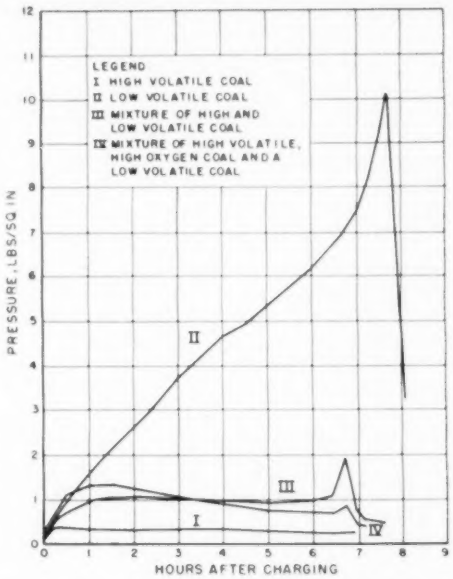

Fig. 6—Typical Russell Oven Expansion Pressure Curves[167]

These explanations of the development of expansion pressure indicate that a number of simultaneous, separate processes are involved in the build-up of gas pressure within the plastic coal, and in the net pressure transmitted to the walls. Consideration of the experimental work which has been performed in the investigation of these variable should permit a more complete understanding of the over-all process.

A. Compressibility of Charge

The probable effect of this factor is the reduction of expansion pressure during the early part of the carbonization period. Compression of the uncarbonized coal between the plastic layers would tend to relieve the gas pressures within the layers by allowing some space for expansion. However, as pointed out by Koppers,[59] there is no possibility of pressure relief in this manner with charges of high bulk density, and after maximum bulk density has been attained with charges of low bulk density. Since no unfused coal exists at the time of meeting of the plastic layers, compression could not relieve the peak pressure, which is the usual criterion by which coals are judged.

Although no experimental evidence has been offered, it is reasonable to assume that the compressibility of particulate coal is primarily a function of the bulk density.[185] Consequently, compressibility could not account for the wide differences which have been observed in the expansion behaviors of different coals; this factor probably contributes to the gradual increase in carbonization of certain coals.

B. Coke Shrinkage

From the results of several different methods of test, the Bureau of Mines concluded that cokes from all coals shrink to practically the same extent (10.5 linear per cent) between formation temperature and 1000° C. Consequently, differences in expansion behavior should be attributed to varying expansions in the plastic layer, rather than to variations in coke shrinkage. Any difficulty experienced in pushing, therefore, should be taken

as evidence of dangerous swelling unless other causes are known to exist.[13]

The above conclusions do not seem to be supported by operational experience, and have not been accepted by several investigators.[61, 130] Soth and Russell[185] found that the coke from a low-volatile coal shrank 9%, and that the coke from a high-volatile (38%) coal shrank 12%. The cokes from coals of 30 and 33% volatile matter shrank to intermediate values, but the shrinkage deviated from a simple function of the coal volatile-matter. The slight inconsistencies were attributed to the experimental difficulty of selecting coke specimens with comparable temperature ranges where the gradient was as high as 300°C per inch.

Continuous coke shrinkage throughout the carbonization period should act similarly to compression of the charge, in relieving the gas pressures in the plastic layers by providing some space for expansion. From the results given above, it may be concluded that differences in the shrinkage of various cokes is at least of a small order of magnitude, and could not account for the extreme differences noted in expansion behavior. Comparative gas and wall pressure measurements, to be discussed later, show that the coke piece is pushed out to the wall during the expansion process, thus minimizing any possible effects of differences in coke shrinkage. On the other hand, coke shrinkage is of obvious importance in the final contraction and resultant ease of pushing of the charge.

C. Existence of Plastic Layers and Plastic Envelope

Plastic envelope formation by advancing plastic layers has been demonstrated by photographs of partly coked box tests[165] and BM-AGA cylindrical retort tests.[156]

Russell showed the presence of a plastic envelope during an expansion test in his movable-wall oven by the indirect method of injecting nitrogen into the center of the charge.[167] Each injection was accompanied by an increase in wall pressure. When injection was discontinued, the wall pressure first dropped below the original value and then gradually increased. This behavior indicated that the envelope was punctured by excessive gas pressure, and that the region of puncture was subsequently sealed over. In addition, runs were made with the top of the plastic envelope kept open by a layer of coke on the coal charge.[87, 168] Expansion pressure curves showed that the pre-peak pressure closely duplicated that for coal alone. However, the peak expansion pressure developed by coal alone was eliminated. (In the example shown, the maximum expansion pressure of 5.8 psi was reduced to 2.6 psi by the breeze covering). Since no reduction in pre-peak pressure was observed, the source of pre-peak pressure must be other than the interior of the plastic envelope. Gas pressure measurements, to be considered in the next section, indicate that the pre-peak pressure is ordinarily due to gas pressure within the plastic layer itself. The elimination of the peak expansion pressure furnished confirmatory evidence that the peak pressure is due to gas pressure within the plastic envelope.

Expansion tests were conducted also in an oven of special design, in which the top part of the chamber (to one foot below the coal line) was widened one inch.[17, 168] By means of a separately controllable horizontal flue, the top flue temperature was maintained at 1325°F, while the bottom was held at 2425°F. These modifications permitted the easy escape of gases from the interior of the charge by retarding coking at the top. The maximum expansion pressure of a mixture of Beckley seam coal and pitch was reduced from more than 12 psi in the regular oven to about 4 psi in the altered oven.

The fact that gas-pressure curves in commercial ovens (Fig. 9) exhibit peak pressures is an indication that plastic envelopes are also present in large ovens.

D. Gas Pressures Within the Charge

The close relationship between expansion pressure and gas pressure within the charge is evident from the course of these pressures during the tests shown in Figs. 7 and 8. The successive increases and decreases of gas pressures in the tubes located at increasing distances from the wall have been interpreted as indicating the progression of the plastic layer past the sampling points. It is evident that, at any time during the pre-peak period, the wall pressure approximated the gas pressure at the sampling point coinciding with the position of the plastic layer. Since the gas pressures in the middle of the charge were low during this period, it must have been possible for the gases formed on the cold side of the plastic layer to pass out of the charge at an area of low resistance. The relative pressures indicate that the pre-peak wall

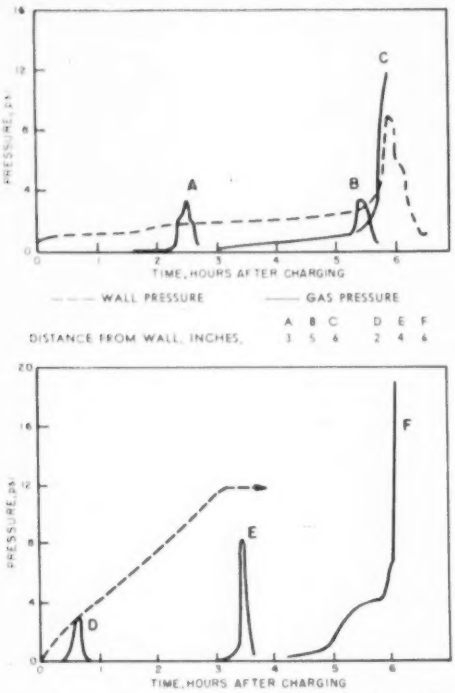

Fig. 7.—Wall and Gas Pressures in Movable-Wall Test Oven[144]

pressures were due to gas pressure within the individual plastic layers, and not from gas pressure within the plastic envelope. It may also be inferred that the expansion pressure of the plastic layer was transmitted by the particles of raw coal on one side, and on the other side was transmitted by the coke to the oven walls.

As the vertical plastic layers approached each other in the midplane of the oven, the gas pressure in the middle of the charge gradually increased. The simultaneous occurrence of maximum wall pressure and mid-plane gas pressure definitely establishes the source of the peak expansion pressure. In most cases, the gas pressure was higher than the wall pressure. This would be expected, since the gas pressure was not effective over the entire wall area because of coking from ends, top, and bottom, while the movable wall measured only a total pressure, from which an average pressure was calculated. In addition, it is probable that the plastic envelope was sufficiently rigid to con-

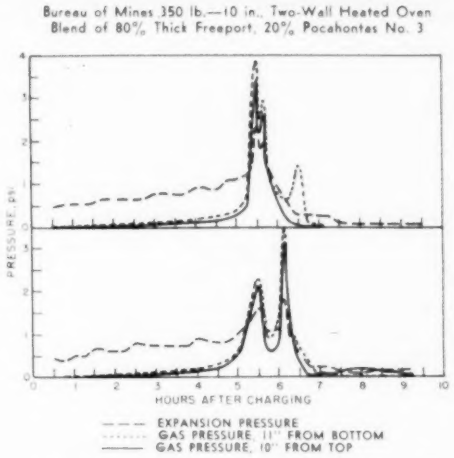
Bureau of Mines 350 lb.—10 in., Two-Wall Heated Oven
Blend of 80% Thick Freeport, 20% Pocahontas No. 3
PRESSURE, psi
HOURS AFTER CHARGING
EXPANSION PRESSURE
GAS PRESSURE, 11" FROM BOTTOM
GAS PRESSURE, 10" FROM TOP

Fig. 8.—Comparative Wall and Gas Pressures[55]

tain a portion of the gas pressure, the remainder being transmitted by the coke to the walls.

Comparison of the pressures at different levels in the midplane of the charge (Fig. 8) indicates that the gas pressure was approximately the same at the top and bottom of the plastic envelope. Release of the gas pressure inside the envelope by allowing gas to flow from the sampling tube was accompanied by a simultaneous decrease in wall pressure,[144] thus furnishing confirmatory evidence regarding the source of the expansion pressure.

On the basis of results from 26 tests, Naugle has shown the following relationship between peak wall and mid-plane gas pressures:[135]

$$\text{Gas Pressure} = 1.95\ \text{Wall Pressure} - 0.83 \qquad (r = .95)$$

The deviations may be partially attributed to experimental difficulties encountered in gas pressure measurement. A number of observers have reported that great care was necessary to avoid erroneous pressure, since the inlet of the gas tube frequently became plugged, particularly during the plastic stage of the coal.

Data concerning the internal gas pressures of a series of coals are available from carbonization tests of some of the BM-AGA coals (Table II). While carbonizing conditions in these cylindrical retorts differ widely from those in ovens of rectangular cross-section, the maximum internal gas pressures should furnish some indication of the relative expanding properties of the different

TABLE II

MAXIMUM INTERNAL GAS PRESSURES

BM-AGA Retorts[154]

Temp. °C			500	600	700	800	900	800	900	1000
Coal	Rank	F.C. dmmf	Max. Internal Gas Pressure, psi							
			13-in. Retort					18-in. Retort		
Pocahontas No. 4	L.V.	83.3	0	51	90	55	67	82	83	35
Upper Kittanning	L.V.	82.1	0	72	65	70	69	66	61	41
Pocahontas No. 3	L.V.	81.7	0	82	88	58	71	62	67	63
Sewell	L.V.	78.7	54	43	21	6	6	6	6	8
Michel	M.V.		—	—	—	—	7	—	—	—
Pond Creek	H.V.A.	66.9	0.9*	1.0*	0.2*	0.1*	0*	0.1*	0*	0*
30% Pocahontas No. 4 / 70% Pittsburgh		68.2						0.65*		
20% Pocahontas No. 4 / 80% Pittsburgh		66.4						0.1*		

*Measured in inches of H_2O and calculated to psi

Commercial Ovens

	Coking Rate in./hr.	Bulk Dens.	Max. Press. in. H_2O	Ref.
Blend, 27.0% V.M.	1.1	Normal	40	202
29.7% V.M.	0.7	"	24	169
18.3% V.M.	0.7	Low	2	178
21.0% V.M.	1.2	"	3	2

coals. The maximum gas pressure usually occurred at about 70% of the coking time. It may be seen that the gas pressure was roughly proportional to the fixed carbon content, the highest pressure tabulated (90 psi) being developed by Pocahontas No. 4 coal carbonized at 700 C. High-pressure coals always expanded the retorts, in some cases to the bursting point, even though these coals were charged at low bulk densities. It was also noted that some retorts were deformed when the internal gas pressure was low, from which it was concluded that other factors contributed to coal expansion.[156]

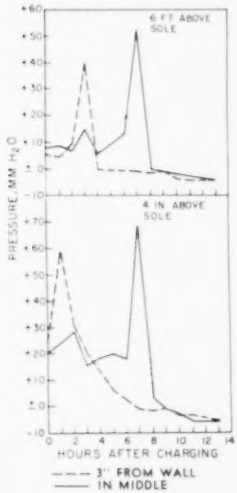

Fig. 9.—Internal Gas Pressures in a Full-Scale Coke Oven[2]

Internal gas pressures measured during carbonization in commercial ovens are also shown in Table II. The maximum pressures were low, presumably because of slow coking rates or low bulk densities. However, the course of the pressures (Fig. 9) were similar to those observed in experimental apparatus.

Gas pressures in the plastic layer and plastic envelope account for the expansion pressures of the coals of most practical interest—those having sufficient plasticity to exhibit peak pressure. However, another type of expansion must be operative for those coals which exhibit a maximum pressure during the early part of the coking period, and little or no peak (Fig. 6, curve IV). Such coals would include those at the limits of the coking band, oxidized coals, and high-inert charges. The pressure from the low-rank and oxidized coals are ordinarily in the safe range, the initial pressure being of the order of 1.5 psi with little or no peak; on the other hand, semi-anthracites may give initial pressures as high as 4 psi and no peak.[144] Since fusion in these coals is poor, it would not be expected that their expansions are due to gas pressure in the plastic layer or plastic envelope. For these coals, the wall pressure is probably due to particle swelling caused by gas pressures within the individual coal particles.

E. Thickness of Plastic Layer

Attempts to measure the thickness of the plastic layer directly by the "feel" of a needle in a laboratory retort have apparently been abandoned because of the personal element involved.

The width of the layer was visually observed in a partially coked charge of Pittsburgh bed coal removed from the Bureau of Mines sole-heated oven.[53] After a coke layer 1½ in. wide had been formed, the plastic layer ranged in thickness from ¼ to ½ in.

The thickness of the plastic layer during carbonization in the Bureau of Mines' small two-wall heated oven was estimated by the indirect method of comparing the temperature progression with the temperature limits of plasticity as indicated by the Davis plastometer.[134] The estimates were made from plots of isotherms of plasticity limits, on coordinates of time and distance from wall. At a heating rate corresponding to a flue temperature of 2400°F, the vertical plastic layers averaged about 0.2 in. in thickness when near the oven walls, then thickened as they approached each other. At the time of meeting of the layers, the double layer was about 1.4 in. thick. At a heating rate corresponding to a flue temperature of 2100°F, the layers were 0.3 in. thick initially, increasing to a double layer 1.9 in. thick. These tests showed that

the thickness of the plastic layers is greater with lower wall temperatures and lower heating rates.

Russell and Perch made similar estimates from temperature progressions in their movable-wall oven, and temperature limits of plasticity as measured with the Gieseler plastometer.[167] The thickness of the plastic layer was defined as the distance in the charge corresponding to the upper and lower temperature limits of plasticity. Geometric considerations prove that the thickness may be calculated from the following formula:

$$\text{Thickness (in.)} = \frac{\text{plastic range (°C)}}{\text{temp. gradient in plastic layer (°C/in.)}}$$

Plotting of the data obtained during the carbonization of a typical coal showed that the thickness of the vertical plastic layers steadily increased from zero at the start of the coking period to 0.5 in. at the sixth hour; at 6.7 hours, the two layers met to form a double plastic layer 1.7 in. wide. Calculations on 25 coals showed that the double layer may be as much as 3.9 in. thick at low rates of heating.

F. Path of Gases from Plastic Layers

The gas-pressure curves in Figs. 7 and 8 indicate that the gases leaving the hot side of the plastic layer may pass through the coke with a negligible pressure drop; the cold side gases frequently encounter enough resistance to build up considerable pressure, most pronounced when the plastic layers meet. Consequently, the relative proportions of gases leaving the two sides of the plastic layer should be considered.

Only a limited number of measurements have been made of these proportions. Schmidt found that, with coals of 19 to 22% volatile matter, from 22 to 28% of the sum of the gas, tar, and ammonia left the cold side of the plastic layer.[178] Foxwell, working with coals of approximately 30% volatile matter, found that from 10 to 30% of the permanent gases were evolved on the cold side.[59]

There are various theories concerning the factors which influence the relative proportions of hot- and cold-side gases. Sapozhnikov concluded that the width of the plastic layer was determinative, since as much as 70% of the total gas was evolved on the cold side when the plastic layer was narrow, and only 10% when the plastic layer was wide.[172] Soth and Russell have proposed the estimation of the relative proportions from fluidity-volatilization relationships (Fig. 2, p. 21). They suggested that the flow to each side varies inversely with the resistance, resistance being defined as the temperature interval enclosing fluidities less than 50 divs. per min. (cross-hatched area in Fig. 2).[185]

Indirect evidence may also be some indication of the path taken by the gases. Smith pointed out that high-boiling products in the gases leaving the cold side of the plastic layer should be condensed in the coal.[23] If a substantial flow of gas has occurred in this direction, the pyrolysis of these deposited tars and oils should cause a sudden enrichment of the gas at the time of meeting of the plastic layers. The gases leaving the hot side travel through the hot coke, where they are cracked to the secondary products. The cold-side gases, however, probably leave the charge through the more permeable layer at the top, where they are cracked to a lesser extent, since the time of contact is very short. Consequently, gas analyses made throughout the carbonizing period should furnish information concerning the path taken by the gases. Data were presented which showed that sudden enrichment of the gas occurred at 75% of the coking time, presumably at the time of meeting of the plastic layers. The results were confirmed by several other workers using different coals and carbonizing chambers (Fig. 11).

Examination of gas analysis-time curves from other sources indicates that this sudden enrichment does not always occur.[102, 203] In addition, analysis of sponge attached to the inner end of coke pieces showed that its ash was the same as the balance of the coke piece, indicating that the sponge was formed from coal and not from condensables.[166] For these coals, most of the oil and tar must have escaped through the coke.

Confinement of the gases within the charge, so that they could escape only through the vertical plastic layer, has developed very high expansion pressures. Experiments of this kind are described by Gieseler, who carbonized charges in a horizontal tube heated by two annular furnaces which were slowly advanced toward each other during the coking period.[71] Some of his results were as follows:

	Bulk Density pcf	Max. Expansion Pressure, psi
Coal G7 (Expanding)	56	47
	62	165
Coal F (Non-Expanding)	56	None
	62	71

Since these pressures are much higher than those observed in ordinary methods of carbonization, it is indicated that the gases within the plastic envelope do not escape through the plastic layer, but leave the charge at an area of lower resistance, probably through the more permeable area at the top of the charge. To increase the yield of hydrocarbons by increasing the flow of gases by this path, Smith covered the coal charge with a two-inch layer of coke breeze.[22] Russell has shown (see **Existence of Plastic Layers**, p. 25), that provision of such a low-resistance avenue of escape for the internal gases by a breeze layer, or other modification, decreases the maximum expansion pressure.

It can be concluded from these experiments that a variable proportion of the total gases are evolved on the cold side of the plastic layer; however, the factors which influence the relative proportions evolved on the hot and cold sides have not yet been defined. It is indicated that the gases within the envelope exit through the top of the charge. Undoubtedly, the restriction of this area as the plastic layers approach each other contributes to the development of peak expansion pressure.

G. Theory of Mechanism of Development of Expansion Pressure

This description, although based on the theories and experimental work cited, should be regarded only as a working hypothesis, since certain aspects are necessarily based on inference rather than direct experiment.

As coking coal passes through the range of carbonization temperature, the simultaneous occurrence of rapid volatilization and softening of the coal substance results in swelling of the particles. The force causing swelling is the pressure of the internal gases, which are partially constrained by the capillary structure of the coal.

Coals Forming Continuous Plastic Layers. In a coke oven, the restraints imposed by the walls, floor, and weight of the superincumbent coal permit the internal pressure to deform the softened particles into a substantially continuous plastic layer, which entraps bubbles of gas. The pressures within these bubbles must rise to a value high enough to enable the passage of the gas from the plastic layer, resulting in a pre-peak pressure upon the oven wall. The greater quantities of gas pass laterally through the coke and upward along the wall, and smaller quantities pass into the coal charge and escape through the more permeable area at the top of the charge.

In the case of the high-expanding low-volatile coals (Fig. 6, curve II), and to a lesser extent the medium-volatile coals, the gas pressures within the individual plastic layers increase as the layers progress toward the middle of the oven. These increases in pressure may be attributed to increasing resistance caused by the gradual thickening of the layers, which reach maximum thickness when they meet in the mid-plane of the oven. At the time of meeting, the rate of temperature rise increases sharply (Fig. 10), due to predrying and

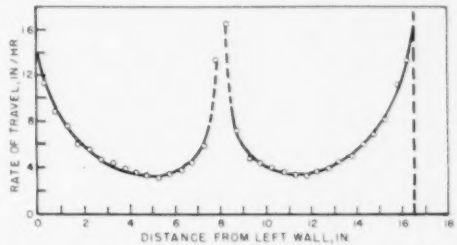

Fig. 10.—Rate of Travel of Fusion Zone in Coke Ovens[169]

preheating of the coal, with a consequent increase in the rate of gas evolution (Fig. 11). (The latter readings were made at hourly intervals; it is probable that readings made at shorter intervals would indicate a sharper peak). At the same time, the area of escape for the gases between the plastic layers is greatly restricted. These factors cause a rapid increase in the mid-plane gas pressure,

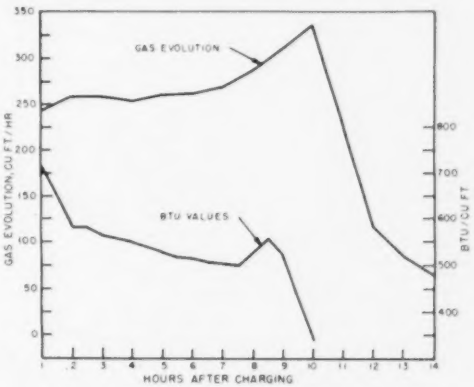

Fig. 11.—Gas Evolution and Btu Value in Illinois Slot Oven[151]

with an accompanying increase in wall pressure. The high pressures continue until the rate of gas evolution is decreased and the permeability of the layer is increased by the progressing carbonization, after which the mid-plane gas pressure and the wall pressure drop to low values.

The high-volatile coals of higher rank have pronounced free-swelling abilities, and produce plastic layers of high fluidity. Since the plastic layers offer no substantial resistance to the flow of gas at any time, pressures remain well below 1 psi (Fig. 6, curve I).

Blends of low- and high-volatile coals develop pressures which are usually intermediate between those developed by the separate coals. With typical blends of this type (Fig. 6, curve III), the plastic layers offer only enough resistance to the flow of gas to give a wall pressure of about 1 psi during the pre-peak period. It appears that a pressure of this order is indispensable for the formation of a strong coke. The pressure will rise to about 2 psi only under the exaggerated conditions present at the time of meeting of the plastic layers.

Coals Forming Non-Continuous Plastic Layers. Coals at the limits of the coking band, oxidized and high-inert charges, and mixtures containing appreciable amounts of these coals (Fig. 6, curve IV) develop maximum pressures during the early part of the coking period, and little or no peak pressure. Since these coals are characterized by low fluidity, poor swelling ability, and poor fusion, it is not probable that carbonization pressure results from gas pressure within either the plastic layer or plastic envelope. The usually low wall pressure may be ascribed to the slight swelling caused by gas pressures within the coal particles themselves. These coals, because of their comparatively open physical structure, do not swell sufficiently to form plastic envelopes offering significant resistance to the passage of gas.

While this type of expansion is of more theoretical than practical interest, initial pressures as high as 1.5 psi are common, with semi-anthracites[114] developing as much as 4 psi.

IV. Present Practice in Expansion Testing

A. Test Apparatus Used

The test-oven most widely used for expansion testing in this country is the Russell oven. This oven carbonizes 400 to 450 lb. of coal in a refractory chamber 12 in. wide, 30 in. long and 42 in. high.[10, 167] Both walls are heated by coke-oven gas burning in flues maintained at temperatures up to 2500° F. (7 to 8 hrs. coking time). One of the walls is stationary; the other is mounted on a carriage and is movable. The movable wall is counterbalanced to overcome friction, and is connected through a lever system to a 1300-lb. weight on a platform scale. The pressure during carbonization is measured by weighing the residual weight at regular intervals. Reproducibility of the test is given as 10%, when conditions of test are constant. Coals which exert more than 2 psi in the air-dried condition are considered dangerous.[165] This oven is also used as a pilot oven for the preparation of experimental cokes. While the properties of the cokes differ slightly from those produced in coke ovens, reliable conversion factors are available.[165] About 21 Russell ovens are in use in this country, and about 6 in foreign countries.

In the Bureau of Mines vertical slot oven, the 350-lb. charge is carbonized in thin-walled steel retorts 27 in. wide and 44 in. high with a nominal width of 10 in. (tests have been run at widths from 6 to 13 in.)[10, 108] Both walls are electrically heated according to a predetermined schedule. A pressure-gage mechanism records the pressure exerted by a constant-volume controller in preventing movement of the movable wall. Results of 36 tests[135] indicated a probable error of 0.4 psi. A bulk density of 50 pcf is recommended.

The Bureau of Mines expansion oven of 17-lb. charge capacity was unsatisfactory under both free and confined-top conditions (Appendix V, F, p. 41).[134] Their newest development is a two-wall heated oven carbonizing up to 1000 lbs. of coal.[34] This oven is 17 in. wide and heated by Globars. A practically frictionless movable wall is assured by suspending the wall from overhead.

A Wilputte testing oven, 18 in. wide and of 675 lb. capacity, has been placed in operation at Lorain, Ohio.[201]

The Bethlehem (Brown) test oven consists of a carbonizing chamber approximately 10½ in. wide, 29 in. long and 4 in. deep, holding about 40 lb. of coal.[10, 35] The temperature of the oven sole flue is maintained at 2350° F by a gas burner. Movement of the superimposed piston is indicated on dial gages. Tests are run at a constant pressure of 2.25 psi and a bulk density of 55 pcf. Coking time is 6 to 9 hrs. Duplicate tests should agree within 2%. Brown states that the allowable expansion limit must be set by each plant and that the coke obtained is suitable for proximate analysis and

physical tests.[82] In this country, three companies employ this tester for all coals used by their coke plants. It has also been used by a number of other coke plants and by the Canadian Bureau of Mines.

The Bureau of Mines sole-heated oven is similar to the Bethlehem oven, except that it is electrically heated and carbonizes a charge 5 in. deep.[108] A constant pressure of 2.2 psi is exerted by the piston, and the change in volume noted with a cathetometer. Coking time is $8\frac{1}{2}$ hr. Results are calculated to a standard charge density of 55.5 pcf or to the expansion of dry, solid coal. On the basis of deviations from the mean for 442 separate tests, the probable error was calculated to be 0.5% on the 55.5 pcf bulk density basis, and 0.8% on the dry, solid-coal basis.[135] The tentative criterion for dangerous coals is a positive expansion at a bulk density of 55.5 pcf.

In the following Section B, it may be noted that Plant L uses criteria of +3% to −4% (at a bulk density of 52 pcf) for their better ovens, and −10% expansion for the older ovens.

The investigation of coal expansion has apparently been pursued more diligently in the United States than in foreign countries. England has recently installed its first Russell oven.[144] Reliance has been placed heretofore upon laboratory tests such as the Koppers A.G. swelling test,[16, 144] and the Nedelmann test. Also, the rise and fall of a plate on top of the charge in the oven are taken as indications of expansion and contraction.[16, 197]

In Germany, laboratory-scale tests are also used. H. Koppers G. m. b. H. uses the Koppers small-scale tester referred to above for control purposes.[107] Interpretation of the data was aided by comparison of the results with those from a medium-scale and a large-scale test (presumably the Koppers 1 kg. sole-heated oven and the two-wall heated coke oven), but the use of the larger apparatus has been discontinued. The Ulrich gage[198] is neither widely used nor highly regarded. Carl Otto and Company G. m. b. H. uses the Bunte-Baum-Hauser method. Mainz and Schwarzmann[123] have described tests with the Koppers laboratory apparatus, and Ussar[199] utilized the Imhof laboratory apparatus. Gieseler carbonized charges in a horizontal tube heated by two advancing annular furnaces to determine the expansion pressure[71] (see **Path of Gases**, page 28).

Among the Russian test apparatus may be mentioned the two-wall oven of 25 lb. capacity used by Kushnirevich.[92] Erkin described an apparatus for measurement of the lateral contraction of the coke during the coking process,[50] and the measurement of vertical settling by noting the movement of a metal disk on top of the coke-oven charge.[51] The Sapozhnikov plastometer, a laboratory expansion tester, is employed for control purposes. Coals are classified according to volatile matter content and plasticity as measured by shrinkage of a coal-sand mixture heated while under the pressure of a weighted piston.[173, 192, 193, 194]

Other methods of test are used in several coke plants, but details have not been published.

B. Plant Practice and Oven Damage in Individual Plants

The available information concerning practices in individual plants, mostly American, is given below. Although complete details are lacking, the data show a wide range of variation in oven design, operating practice and interpretation of test data. These are further discussed in the following Section C.

Plant A[82] — On the basis of their experience over the past 25 years with coking coal mixtures which exert wall pressures estimated at 3 to 5 psi, the operators feel that the limitation of pressure to 2 psi, as advocated by Koppers, need not be adhered to. This plant carbonizes a mixture of 30 to 40% Pocahontas, the remainder high-volatile, at a coking rate of 1.15 inches per hr. in old Koppers batteries. Batteries and many walls were rebuilt in the past. However, since controlling the bulk density in the oven at 48 to 49 pcf by addition of water to maintain the moisture content at 5%, no more walls have had to be replaced. Russell oven tests showed pressures of 7.4 psi on the air-dried coal, and 1.2 psi at 4.5% moisture.

Plant B[82] — This plant consists of a battery of old Koppers ovens carbonizing a mixture of 25% Lower Kittanning and 75% higher-volatile, and a battery of Koppers Underjet ovens on a mixture of 35% Lower Kittanning and 65% high-volatile. The coking rate is 1.05 in. per hr. One battery has operated 26 years with no repairs to walls. Bulk density in ovens is 48 to 49 pcf. Russell oven tests showed pressures of 3.5 to 4.9 psi.

Plant C[82] — Batteries range in age from 3 to 26 years, and all are in good condition. Coal mixture is 25% Pocahontas plus 25% Preston plus 50% high-volatile, charged at an oven density of 49 pcf by maintaining 4.5% moisture. Coking rate on old

batteries is 1.05 in., and on the new battery is 1.20 in. per hr. Russell oven tests showed a pressure of 4.1 psi.

Plant D[52] — Of the two batteries at this plant, No. 1 had been in service 17 years, and No. 2 14 years. They were formerly operated on a mixture of 40% Upper Kittanning and 60% Pocahontas, at a pulverization of 55% minus 1 8-in. After 8 and 5 years of service, respectively, both batteries developed pushing troubles, followed by spalling, especially on the bottle brick ends. The damage was particularly noticeable on the No. 2 battery, underfired with blast-furnace gas. The trouble was overcome by reducing the low-volatile coal to 35% and increasing the pulverization to 80%. Later the older battery was put on a 47% low-volatile mix. No. 1 Battery has had no walls rebuilt, but No. 2 has had 50. The oven bulk density was 48 to 49 pcf, with moisture maintained at 6%. The coking rate on the older battery was 1.23 in. per hr., and 0.97 on the newer. Russell oven tests on No. 1 Battery mixture showed pressures of 8.0 psi on air-dried coal, and 1.0 psi at 6% moisture.

Plant E[52] — This plant consisted of two Koppers-type batteries built 27 years previously, and one Becker-type battery built 18 years previously. When operated on a mixture of 15% Lower Kittanning and 85% Thick Freeport, the ovens often pushed hard, but there were no stickers. Increase of the low-volatile coal to 20% caused stickers to develop. The low-volatile coals were tested in a movable-wall (Koppers-type) test oven, and those coals were eliminated whose blends (20% low-volatile to 80% high-volatile) developed more than 2 psi pressure. After this elimination, the low-volatile percentage was increased to 20%, with easier pushing than had formerly been the case with 15%. Present practice allows a pressure of 2 psi on the moist, blended coal. The average oven width is 18 in., with a $1\frac{1}{2}$ in. taper. No walls have been rebuilt, and no spalling has occurred, but walls are bowed, particularly on the Becker-type battery. Coking rate is 1.1 in. per hr.

Plant G[52] — "This plant uses 65% low-volatile coal. Expansion pressures are high, and the average oven life is about ten years. It has been a matter of economics at this plant to use large amounts of low volatile coal and obtain maximum coke yields, even at the expense of a reduction in battery life."

Plant H[52] — The plant consisted of 3 batteries of Koppers ovens built 26 years previously, and a Becker battery built 14 years previously. The Koppers ovens are of 17-in. average width, and $2\frac{1}{2}$ in. taper. There are six coal mixing bins in use. No expansion tests have been made on the hundreds of coals which have been used. An unknown coal is first coked in can tests; if results are favorable, the coal is added to the mix in an amount equal to 10% of the mix, and the percentage gradually increased to 20. The plant has not had a sticker in years. There have been no oven failures, and no patching has been done except for occasional spalls due to spray trouble.

Plant I[52] — This plant produced foundry coke on a long coking time, using a 50-50 mixture of high- and low-volatile coals. Serious trouble was encountered and the battery was rebuilt.

Plant J[52] — A blend of 60% high-volatile and 40% low-volatile damaged the ovens.

Plant K[52] — This plant consisted of a battery of Koppers ovens 13 ft. in height, built 6 years previously, and older batteries 12 ft. and 10 ft. in height. The blend contained 21% low-volatile, and showed an expansion pressure of 3.5 psi at a bulk density of 53.7 pcf in the Russell oven. After six months of operation, the new battery developed spalling on the coke side between the second and third flues, although there were no stickers. The coal blend used on this battery had been satisfactory on the older, lower ovens. After the elimination of coal from one mine, spalling was markedly decreased.

Plant L[52] — Highly expanding coals in amounts up to 50% of the blend were used in the production of foundry coke on a long coking time. At the slower coking rate, no wall damage was noted. To avoid blends causing stickers, it was found necessary to determine actual coal expansion with a modified Bethlehem tester. Satisfactory blends varied from 3% expansion to 4% contraction. Old ovens used for domestic coke require a mixture showing 10% contraction, due to irregularities in the walls.

Plant M[52] — For $3\frac{1}{2}$ years a blend of 35% Pocahontas No. 3 and 65% Elkhorn had been carbonized, the blend developing an expansion pressure of 3.4 psi in the Russell oven. During this period there was no spalling, but some brick deformation occurred on the first row of liners at both the coke and pusher sides of the batteries, between

the door liner brick and the wall liners, from 3 to 6 ft. above oven floor. Increase of the Pocahontas to 36% for 18 days caused hard pushing, many "pull-backs", and some stickers. The trouble was worse on the batteries with 2 in. taper than on those with 2½ in. taper. Oven bulk density was 48.3 pcf, and flue temperature 2363° F at air port.

Plant N[16] — This English plant, using compressed charges of low-ash coal, suffered severe wall damage from expanding coals. After adopting the Koppers laboratory tester for control purposes, it was found that charges should be limited to an expansion of less than 1.0% and a final contraction of more than 5.7% at a bulk density of 65 pcf. Measurements of the rise and fall of a plate on top of the charge in the oven were also made. The limits set for the older ovens were 2.3% maximum expansion and 2% minimum contraction; for the newer ovens, 1.2 and 4.5%, respectively.

Plant O[85] — The expansion properties of coals are measured by heating about three pounds of coal in a sheet-iron box, the charge being covered with a plate weighing ten pounds. Observations are made to determine whether the plate is raised or lowered during heating.

Company P — Both the Brown and Russell test ovens are used in selecting coals for carbonization in the various plants. The criteria for the Brown tester vary from 9 to 5% contraction, depending upon the width of oven and coking rate to be used.

C. Interpretation of Expansion Test Data

Consideration of the plant data given above shows that many plants successfully operate on coal blends which give expansion pressures considerably above the recommended limit of 2 psi, with no apparent deleterious consequences, such as spalling and stickers. The interpretation of expansion test data has been a controversial subject in the coke oven industry, and some clarification is needed. No claims are found in the literature that any of the test methods in use exactly duplicate the pressures exerted in a coke oven. The limited data which have been obtained by direct measurement of expansion pressures in plant-scale ovens show that these pressures are of the same order of magnitude as the pressures measured in large-scale test ovens heated from two sides. As an example, the Ulrich gage showed pressures of from 1.3 to 2.3 psi in commercial ovens,[139] while tests in the Russell oven on air-dried samples of blends commonly used in coke ovens showed pressures of about 1.5 psi at bulk densities usually 53 to 54 pcf.[165] (These pressures may be compared with those of representative charges in the Bureau of Mines vertical slot oven, shown in Table X, page 54).

On the basis of their experiences with a large number of coals, the Koppers Company has stated that any air-dried coal or mixture which produces more than 2 psi when tested in the movable wall oven by the prescribed procedure is dangerous to use in coke ovens.[165] The limit is placed at 1.5 psi for ovens more than 10 ft. in height. These clearly-defined limits are the only clear-cut criteria which are known to have been proposed, and consequently are of great value to the industry.

The plants owned by Koppers are all operated on blends which develop a maximum pressure of 1.5 psi or less. Some of their batteries have operated for as long as 27 years, and no major brick relining has been necessary.[82]

Koppers' expansion pressure limitation was based largely on observation of oven damage in three plants, from five to nine years old. All three plants developed spalling of the oven walls, hard pushing, and stickers. In one battery, this trouble resulted in such complete failure that it had to be rebuilt. Investigation of the coal charges showed that they developed pressures of from 2 to 3.5 psi. Further evidence was found in the experience of two other plants which developed spalling, but no hard pushing or stickers. In both plants the coal mixture was changed in conformance with expansion-pressure limits, and no further spalling was noted.[82]

A study of operating conditions at the plants using charges with expansion pressures above the limits specified will show the presence of mitigating factors. For example, Plant A controlled the moisture and bulk density by spraying water on the coal, thus maintaining 5% moisture in the coal, as determined by hourly determinations. Plants B and C also maintain low bulk densities by spraying water on the coal, although the additions are not controlled by frequent moisture determinations. At Plant D, an exceptionally high moisture content of 6% is maintained by the use of a wet-washed low-volatile coal of approximately 8% moisture. The uniform heating obtained by underfiring with blast-furnace gas appeared to accentuate the wall damage. The 1½ in. taper of the ovens in Plant E would tend to cause pushing dif-

ficulties. Plant G apparently considers it profitable to sustain some oven-wall damage in order to obtain maximum coke production and the coke properties attending the use of a blend containing 65% low-volatile coal. In Plant H, the limitation of any one coal to 20% of the blend, and the mixing with five other coals appears to neutralize the expanding effect of the coals received. The experience of Plant K indicates that higher ovens aggravate the damage from expansion. It will be noted that Plant L is on a long coking time. At Plant M, the $2\frac{1}{2}$ in. taper was found to be more satisfactory than the 2 in.

From the above examples, it is reasonable to assume that the conditions peculiar to the individual plants may offset the excessive pressures shown by expansion tests. The cases cited do not include all factors to be considered in applying the 2 psi limit. A more complete listing would include:

1) The bulk density of the charge in the oven, and the limits of its control.
2) Limit of accuracy in making up coal blends.
3) Dimensions of oven, especially width, height, and taper.
4) Present condition of ovens.
5) Over-all flue temperature and limits of control; temperature differential in flues.
6) Pushing series, and how closely it is followed.
7) Expected variability of expansion pressure in coals.

It is evident that there are certain reservations which must be applied to a definite allowable maximum pressure obtained by a test method. Koppers' limits were presumably set up for ordinary operating conditions in ordinary plants, making due allowance for a factor of safety. Exceeding of the limits may be considered if it is definitely known that the peculiar features of an individual plant or method of operation will restrict the expansion pressure in the coke oven to a safe figure.

V. Influence of Variable Carbonizing Conditions Upon Expansion

The factors affecting expansion may be classified as: 1) those dependent upon the conditions under which the coal is carbonized; and 2) those due to the constitution (both chemical and physical) of the coal itself.

The factors of the second group can be properly evaluated from the heterogeneous data available only when the influences of the physical condition of the coal and carbonizing conditions are considered. In the following discussion the attempt is made to assess the relative influences of the factors affecting the expansion of coal.

A. Bulk Density

The relationship between maximum expansion pressure and bulk density was expressed by the Bureau of Mines by plotting the log of the pressure vs. the log of the fraction of the charge volume occupied by solid coal.[55] The latter term equals the bulk density divided by the true density. For two series of tests on different coals, the data were approximated by straight and nearly parallel lines.

The data plotted in Fig. 12 (also Fig. 31, p. 46) show that the relationship may be expressed more simply by plotting the log of the expansion pressure vs. the bulk density. Each series of results is approximated by a line of the slope shown, 0.10.

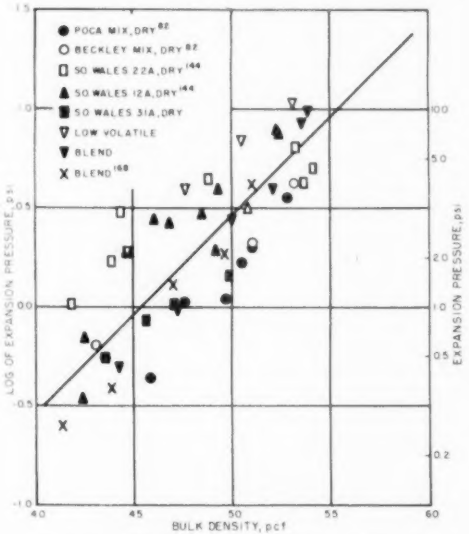

Fig. 12.—Effect of Bulk Density on Expansion Pressure in Russell Oven

This relationship is valid whether the bulk density is varied by adjusting the moisture or pulverization of the charge, or by mechanical compression. While some of the deviations from the general slope may be real, it must also be recognized that they are at least partly due to experimental error. Difficulties are likely to be encountered in the preparation of identical samples, maintaining

standard conditions during the expansion test, and measuring the bulk density of the charge. This experimental error in a large portion of the published literature does not permit close correlation of expansion data, but with sufficient data it is possible to show broad trends.

The relationship between the volume expansion in a sole-heated oven and the bulk density may be expressed by a simple equation. It has been observed that the calculated expansion of the dry, solid coal was substantially constant at varying bulk densities.[12] The dry, solid-coal expansion was calculated from the following equation:

$$E_s = \left[\frac{SG \times 62.4 \times (100 + E_f)}{BD} \right] - 100$$

E_s = dry, solid coal expansion, %
E_f = volume expansion at test bulk density, %
SG = true specific gravity
BD = test bulk density (dry), pcf

The slight deviations of experimental results from the above equation were ascribed to changes in the rate of heating caused by large differences in bulk density, even at constant flue temperatures.

From the above expression the following equation was derived for calculation of expansion results to a standard bulk density (now 55.5 pcf):

$$E_x = \left[\frac{W_x}{W_f} (100 + E_f) \right] - 100$$

E_x = volume expansion at W_x bulk density, %
E_f = volume expansion at W_f bulk density, %
W_x = standard bulk density, pcf
W_f = test bulk density, pcf

A similar expression solved for E_f shows that the percent expansion is a direct function of the bulk density.

Of the many factors which affect the bulk density of the coal charge in place in the oven,[143] only the more significant will be discussed here. Practically all experimental data have been obtained with small-scale testing methods, where conditions are far different from those prevailing in large-scale operation. The relationships presented by the Bureau of Mines between bulk densities by three testing methods and average densities in coke ovens are shown in Fig. 13. The dropped-coal method gave results closely approximating those observed in practice. Both the ASTM and Koppers-cone methods gave lower bulk densities than those observed in coke ovens and exaggerated the influence of moisture; it is probable that the influence of other variables would also be exaggerated. However, the trends for the various variables shown by these two methods of test should be indicative of the changes which would occur in practice.

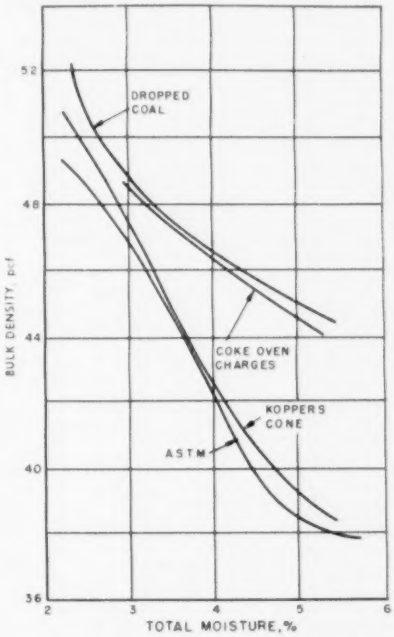

Fig. 13.—Comparison Between Bulk Densities in Full-Scale Ovens and Those Determined by Three Methods of Testing[14]

1. Size Consist. Brough investigated the effects of different types of grinding equipment, relative particle size, and size distribution upon the ASTM bulk density of air-dried coal.[33] The screen analyses of 22 samples were represented with fair accuracy by parameters of Bennett's modification[15] of the Rosin-Rammler equation:

$$R = 100\, e^{-(x/\bar{x})^n}$$

R = cumulative percentage by weight of material larger than x
e = base of natural logarithms
x = size of particle, mean projected diameter
$\bar{x}$ = absolute size constant
n = distribution constant

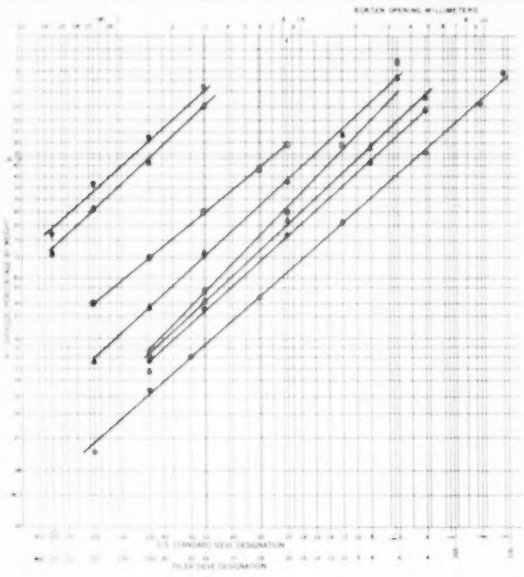

Fig. 14.—Typical Screen Tests on Rosin-Rammler Co-ordinates[33]
(Graphical Form by courtesy of Bureau of Mines)

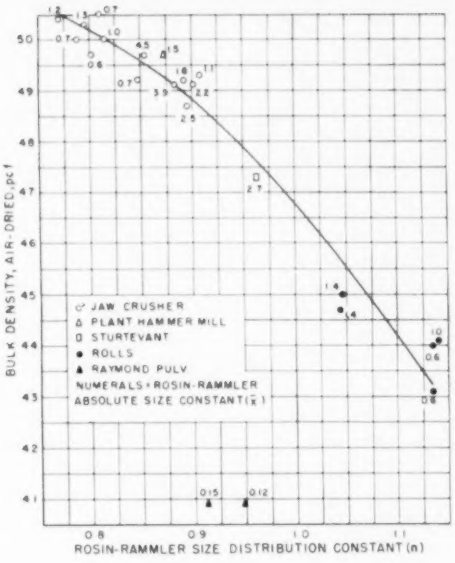

Fig. 15.—Effect of Size Distribution on Bulk Density of Air-Dried Coal[43]

Typical screen tests plotted on Rosin-Rammler coordinates are shown in Fig. 14.

The results, summarized in Fig. 15, show that a rather narrow range of bulk densities was obtained with each type of grinding equipment. The bulk densities of the 20 samples of larger particle size (from 53 to 97% minus $\frac{1}{8}$ in.) could be correlated with the size distribution parameter "n", no trend being evident for particle size or differing particle shapes. For the range of sizes specified, which includes the pulverizations ordinarily used in practice, it is apparent that size distribution is the dominant factor governing the bulk density of air-dried coal.

The unusually low bulk densities exhibited by the two finely pulverized samples shows that in this range of particle size the absolute size is the dominant factor. This dependence of bulk density upon particle size is in accordance with the findings of Roller,[100] who showed that particle size was of no significance in the bulking of powders until the size was reduced to a "critical diameter." The low bulk densities of fine powders have been attributed to electrostatic forces and to the high internal friction caused by the large number of points of contact.

2. Moisture Content. Addition of water to twelve of the samples[43] discussed above gave the results shown in Figs. 16, 17 and 18. Fig. 16 represents samples of moderate size variation at substantially constant size distribution; Fig. 17, small size variations with large variations in size distribution; and Fig. 18, large size variations over a small range of size distribution. Since the most consistent spread of data was exhibited by Fig. 18, it was indicated that the minimum bulk density, and moisture content at minimum bulk density, were largely a function of the particle size. Plotting of the minimum bulk densities of all the samples vs. the particle size (Fig. 19) showed the close relationship between these two quantities, from which it was inferred that surface area was the significant factor. Calculation of the moisture per unit of calculated surface area enabled the relationships shown in Fig. 20 to be made. All samples reached a minimum bulk density at about 0.13% moisture per surface factor. The tentative interpretation of this behavior is that the frictional re-

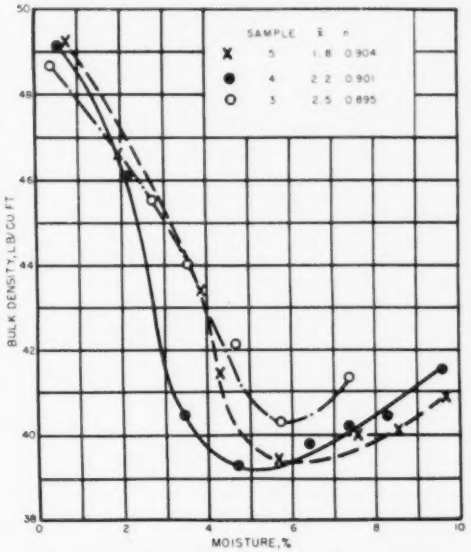

Fig. 16.—Effect of Moisture on Bulk Density[143]

sistances between particles reach a maximum at this concentration of moisture on the surfaces of the particles.

The work cited indicates that, in practical size ranges, the particle size distribution governs the bulk density of dry coal, the wider spreads of sizes giving the higher bulk densities. Because

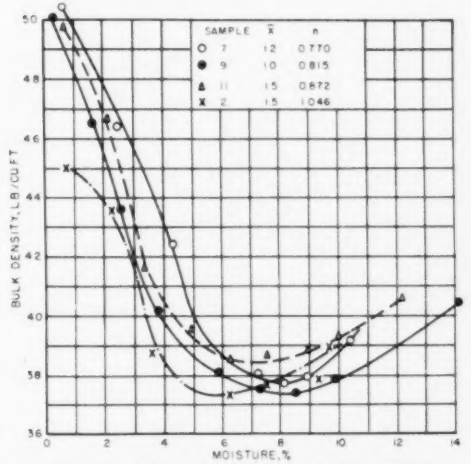

Fig. 17.—Effect of Moisture on Bulk Density[143]

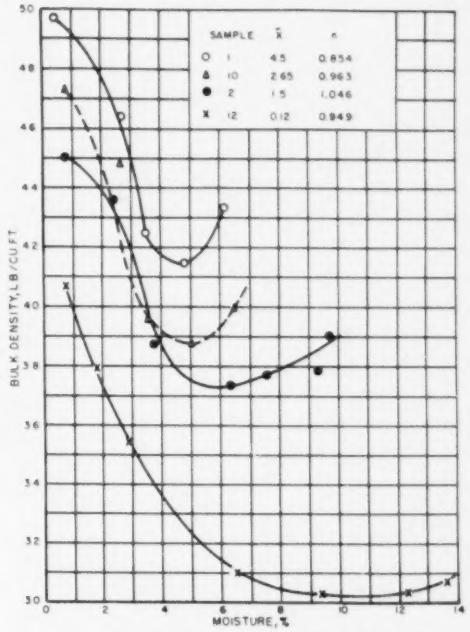

Fig. 18.—Effect of Moisture on Bulk Density[143]

of its relationship to surface area, particle size is of significance to the bulk densities of wet coals. The smaller the particle size, the lower the minimum bulk density, and the greater the moisture content at minimum bulk density.

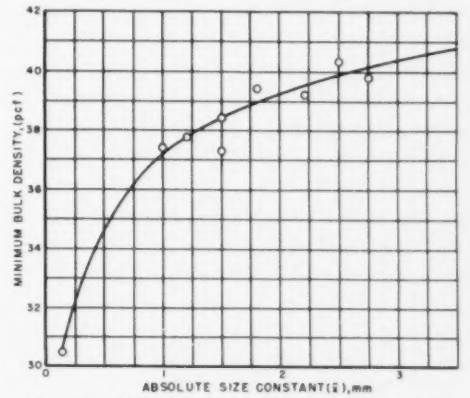

Fig. 19.—Effect of Particle Size on Minimum Bulk Density of Wet Coal[33]

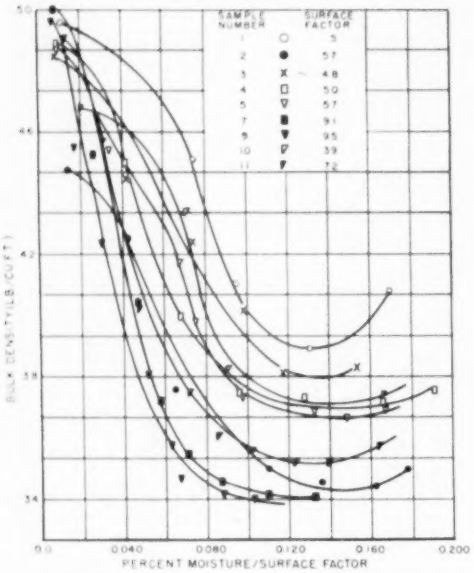

Fig. 20.—Variation of Bulk Density with Moisture per Unit of Surface Area[33]

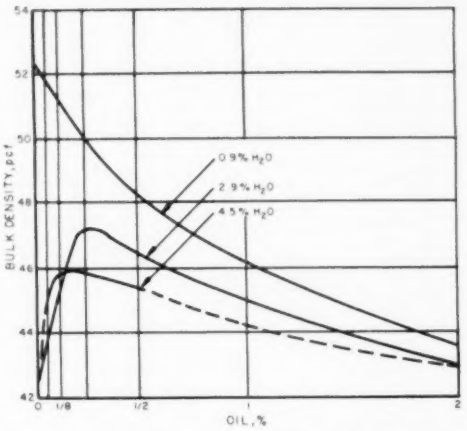

Fig. 21.—Effect of Addition of Oil on Bulk Density[150]

3. Miscellaneous Additions and Treatments. The effect of small additions of oil upon bulk density has been demonstrated by Ramsburg and McGurl (Fig. 21). The oil decreased the bulk density of dry coal, and increased that of wet coal, thus reducing the variations in bulk density due to moisture fluctuations. Similar results have been obtained by other investigators.[4, 40, 91] The equalizing effect of oil is of great value to consistent coke oven operation where varying moisture contents are encountered in the coal as received or as reclaimed from storage.

Automatic devices are available for regulating the flow of oil, or water if necessary, for maintaining any desired bulk density. The device described by van Ackeren[1] automatically determines the bulk density and adjusts the flow of oil or water accordingly.

It would be expected that wetting agents would produce an effect similar to oil. However, experiments with agents of this kind have shown that they do not exert any significant or consistent influence, and definite conclusions cannot be drawn from their behavior.[40, 98, 181]

Changes in the physical state of the water have important effects upon the bulk density. Russian investigators[5] report the following results from tests made on normal and frozen coals:

Temp. C	Bulk Density, pcf
20-24	39.6
0	47.4
-9	48.6

Hygroscopic agents, such as lime, to the amount of 1 to 2%, increase bulk density by 8 to 12%.[3] Starch is also effective.

4. Charging Conditions. The effect of height of fall upon bulk density is shown in Fig. 22. Increases in drop height always resulted in increases in bulk density. This principle is utilized in a German charging machine[106] which allows the coal to fall 15 ft. from a hopper through guiding slots into the oven, giving a bulk density 15% greater than normal. A free fall of 25 ft. gave a 25% increase.

That the bulk densities throughout an oven are not uniform has been shown by Koppers and Jenkner.[88] Maximum bulk densities were found near the sole, and the next highest under the charging holes, particularly on the coke side. The latter

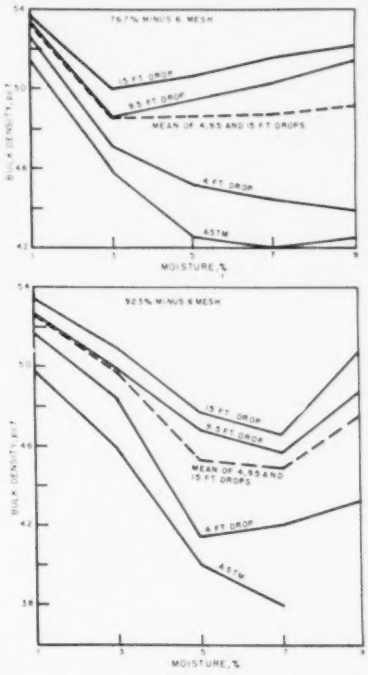

Fig. 22.—Effect of Height of Fall on Bulk Density[181]

densities were dependent upon the sag of the levelling bar, number of passes, and the amount of coal charged. The regions of maximum bulk density correspond with the regions of initial wall failure.

5. Mineral Matter Content. The effect of mineral matter upon bulk density may be judged from the data plotted in Fig. 28, p. 45, which shows bulk densities in the Bureau of Mines slot oven. The two exceptionally low points in this graph are due to the addition of water. The slope of the average line shown corresponds to the generally accepted variation of .010 in specific gravity per 1% difference in ash.

B. Particle Size

Aside from the effect of particle size upon bulk density, some data is available concerning the influence upon expansion of particle size itself. Measurement of the expansion pressures of a coal blend at varying pulverizations indicated that finer pulverization leads to decreased pressures.[82] However, when the pressures are calculated to a standard bulk density, the apparent effect of finer pulverization is to slightly increase the calculated maximum expansion pressure:

% — 1/8 in.	Bulk Density	Expansion Pressure, psi	
		Test	Calc. to B.D. of 54
60.2	55.4	4.8	3.5
83.5	53.7	4.2	4.5
92.6	52.5	3.7	5.2

That the effect of particle size is rather small may also be inferred from the Pontypridd tests.[144] Although these tests were run at coal pulverizations ranging from 6 to 49% minus 1/8 in., no consistent change in pressures with pulverization could be noted.

Volume expansion is slightly increased by finer pulverization. From 31 results obtained with the sole-heated oven, Naugle[155] calculated that a 10% increase in pulverization (% minus 4-mesh) increased the dry, solid-coal expansion 2%.

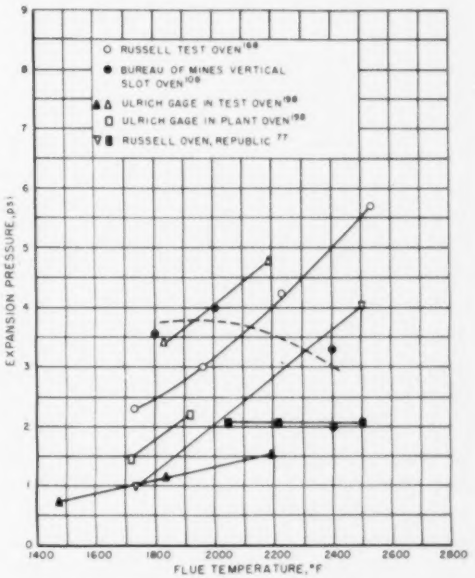
RUSSELL TEST OVEN[68]
BUREAU OF MINES VERTICAL SLOT OVEN[109]
ULRICH GAGE IN TEST OVEN[98]
ULRICH GAGE IN PLANT OVEN[98]
RUSSELL OVEN, REPUBLIC[77]
EXPANSION PRESSURE, psi
FLUE TEMPERATURE, °F

Fig. 23.—Effect of Rate of Heating on Expansion Pressure

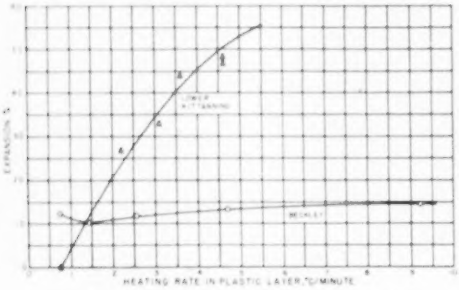

Fig. 24.—Effect of Rate of Heating on Volume Expansion[11]

C. Rate of Heating

The effect of rate of heating, as represented by flue temperature, upon maximum expansion pressure is shown in Fig. 23. Similar observations on volume expansion at various rates of heating in the plastic range are shown in Fig. 24.

In general, increases in the rate of heating led to higher expansion pressures or larger volume expansions. However, there are other data[144] which indicate that peak expansion pressures attain a maximum at about 2300° F. In explanation of the inconsistent effect of rate of heating, it should be pointed out that all coals do not react in the same manner, since complex changes are involved. Faster rates of heating would obviously increase the rate of gas evolution, which would tend to increase expansion pressure. On the other hand, the thickness of the plastic layers would be decreased, and the fluidity would be increased, both of which would tend to decrease expansion pressure.

D. Oven Width

The results of three series of tests concerning this variable are shown in Fig. 25. This (and other) evidence indicates that the expansion pressures of the more highly-expanding coals decrease as the oven width is increased from 6 to 10 or 12 inches. For widths of more than 12 inches, the evidence is not so clear. Of five coals tested in the Pontypridd oven at 12 and 16¾ in. oven widths, one coal decreased, one was neutral, and three increased in pressure at the wider width.[144]

In connection with oven width, the behavior of very thin layers of coal should be mentioned. Taylor carbonized eight coals in an apparatus which

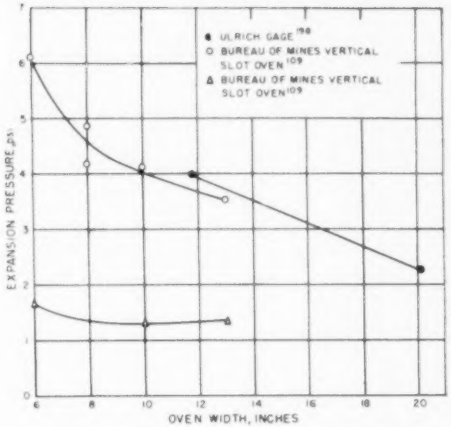
ULRICH GAGE[190]
BUREAU OF MINES VERTICAL SLOT OVEN[109]
BUREAU OF MINES VERTICAL SLOT OVEN[109]
EXPANSION PRESSURE, psi
OVEN WIDTH, INCHES

Fig. 25.—Effect of Oven Width on Expansion Pressure

used a charge only 2 mm. in thickness.[195] The charge was contained in a cylindrical tube, which contained a piston resting on the top surface of the coal. The volume of the charge was kept constant by adding weights to a platform atop the piston rod during carbonization. Ports for the escape of gas were provided by the perforated bottom of the retort. Although none of the coals tested had been observed to damage oven walls, five of them developed pressures of more than 100 psi.

The explanation for the non-consistent effect of changes in width of the carbonization chamber upon expansion pressure is probably to be found in the relationship between rate of heating, discussed above, and oven width (the coking time has been found to vary approximately with the 1.8 power of the oven width[190a]). With wider ovens, less heat would be transferred to the middle of the charge at the time of meeting of the plastic layers, because of the resistances imposed by the long coke pieces. From the discussion in the preceding section, this lowered rate of heating may either decrease or increase the pressure, depending upon the relative influences of the other factors mentioned.

E. Heating Conditions

In Fig. 26 are shown the results of two investigations concerned with the effect upon expansion pressure of heating one wall or two opposite walls.

To attain comparable carbonizing times, the width of the coal layers for the one-wall tests was reduced to one-half that for the two-wall tests, in both cases. In the Russell-oven test, there was probably some conduction of heat from the refractory end-wall and door. In the Bureau of Mines test, conduction from the end-walls was minimized by the use of reversible insulating slabs, the cold sides of which were turned inward just before the charge was inserted. This difference in procedure may possibly explain why a greater difference in results for the two methods of heating was shown by the Bureau tests than by the similar Russell tests. In both cases, however, the expansion pressure for one-wall heating was significantly lower than for two-wall heating, and the characteristic peak pressure was obtained only by the latter method.

Expansion tests for one-wall heated ovens are ordinarily conducted under constant-pressure conditions (2.2 psi) rather than under the constant-volume conditions maintained in the above tests. Attempts to correlate Bureau of Mines data on volume expansion in the sole-heated oven and expansion pressure in the slot oven have proved disappointing. Unfortunately, the available data are confined mostly to coals contracting in the sole oven and to those showing low pressures in the slot oven. In Appendix VI it will be shown that positive expansion data from the two methods of test can be correlated with the same coal properties, indicating that there is some relationship between the two methods of test for expanding coals. This would imply a relationship between expansion pressure and volume expansion for one-wall heating, and a relationship between pre-peak and peak expansion pressures for two-wall heating.

Brown also states that there is no relation between per cent expansion and expansion pressure, since even contracting high-volatile coals show slight peak pressures in a two-wall heated oven.[82] However, the coals giving higher percentages of linear expansion in sole-heated ovens show higher expansion pressures in two-wall heated test ovens.

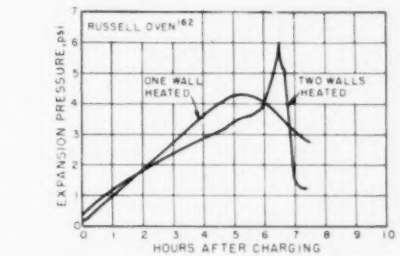

Fig. 26.—Influence of Type of Heating upon Expansion Pressure

F. Relative Size and Shape of Testing Equipment

Small scale ovens (such as described by Altieri[6, 7, 101] and Gauger[69]) which carbonize from 5 to 11 lbs. of coal have not been extensively adopted for expansion testing. The Bureau of Mines has issued a complete description of their experiences with an expansion oven of this size.[134] The oven is 12 in. long, 5 in. wide, and holds about 17 lbs. of coal when filled to a depth of 9½ in. Previous work (see **D, Oven Width**) had shown that maximum wall pressures decreased more or less regularly as oven width increased; consequently, a comparatively high wall pressure was expected, but it was hoped that results could be correlated with those from larger-scale apparatus.

This oven was operated under both free-top and confined, cooled-top conditions, but satisfactory reproducibility could not be attained, and no correlation could be attempted. The authors advance the theories that lack of reproducibility was probably due to rupture of the plastic envelope at varying pressures in the case of the free-top tests, and variable cooling in the confined, cooled-top tests. A photograph of the mid-plane of the charge showed extensive coking from side-walls, top, and bottom.

The difficulties encountered here are those inherent in scaling down any large-size process, namely, in constructing a model of such dimen-

sions that the process is exactly reproduced on a small scale. Obviously, the width of the plastic layer can not be scaled down. The effect of such variables as different degrees of coking from top, bottom, and end-walls can be only a matter of conjecture at the present time.

G. General Considerations

The effect of a number of variables upon coal expansion has been considered for the simplest possible conditions, that is, where the attempt was being made to vary one of the test conditions while holding the other variables constant. Actually, this is not possible for all combinations, since it is evident that the variables are in many cases interdependent. However, the apparent effects of these variables are of sufficient magnitude to greatly alter the expansion pressure of a particular coal.

It is fortunate that the effect of the most significant of these variables, bulk density, is sufficiently consistent for the development of methods for the conversion of expansion data to a uniform bulk density basis. In the case of volume expansion, the validity of these methods has been demonstrated over wide ranges of bulk density. Since the relationship between expansion pressure and bulk density has not been so extensively investigated, the application of the proposed conversion method should be tentatively limited to comparatively short ranges of bulk density. The relationships which have been developed will be utilized in correlation of expansion data in the next section.

The variables relating to rate of heating involve such complexities that no mathematical methods have yet been developed, and only general statements can be made. However, it appears that expansion behaviors may be compared over reasonable ranges of flue temperature and oven width with small error.

VI. Influence of Coal Properties Upon Expansion

In this section are presented the correlations which have appeared in the literature between expansion behavior, under constant testing conditions, and the coal properties considered most pertinent to expansion. In addition, it was found necessary to correlate some of the published expansion data to determine the significance of the various coal properties, and the limits of their application to coal expansion.

A. Chemical Composition

1. Indications of Rank (volatile matter, fixed carbon, or carbon content). A number of investigators have shown the relationship between the expanding properties of coal and the properties usually used as a basis for coal classification.

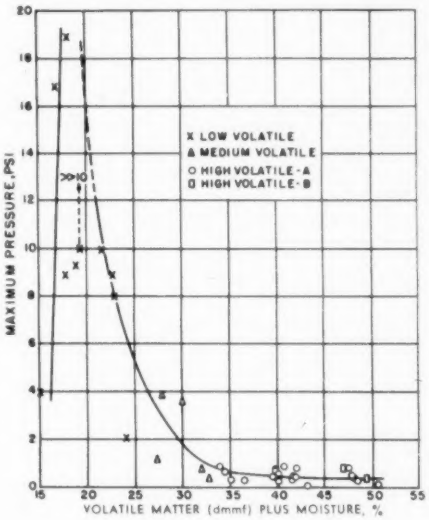

Fig. 27.—Expansion Pressures of Unblended Coals in Russell Oven[41]

Brown related the volume expansions of coals, as measured in his Bethlehem sole-heated oven, with the volatile-matter contents on the dry and ash-free basis.[34, 35] A different curve or straight line was used for each of the coal beds correlated.

The Pontypridd Test Plant Committee has shown the relationship between maximum expansion pressures (as measured in a modified Russell oven) and the carbon contents of some seventy English coals.[111] The correlation in general is poor, although the pressures appear to reach a maximum at about 92% carbon.

Russell and Perch correlated the maximum expansion pressures of unblended coals, as tested in the Russell oven, with the ratio of the moist, mineral-matter-free Btu to the dry, mineral-matter-

free volatile matter (Fig. 1, p. 20). This ratio in turn was correlated with the sum of the dry, mineral-matter-free volatile matter and the total moisture. In another paper,[141] the maximum expansion pressures were plotted directly against the latter sum, and data on several English coals, presumably from Ref. 144, were added to the extreme low-volatile group (Fig. 27). It may be noted that these new data displaced the peak slightly to the left.

As a part of the present study, the following equation was found to indicate expansions of 22 coals, as measured in the Bureau of Mines sole-heated oven:

$$\text{Expansion, } \% = 2.95\ (C^{*}\text{-}80) - 6.82 \log \text{Fluidity} - 1.87\ \text{Ash}_K - 1.42 \qquad (r = .92)$$

(Expansions calculated to a wet bulk density of 55.5 pcf.).

C^{*} = carbon, dmmf, corr. for CO_2, %
Fluidity = Gieseler, maximum, dial divs. per min.
Ash_K = ash in coke, %

Naugle and co-workers expressed the results of 83 expansion tests in the same apparatus by the following equation:[135]

$$\text{Expansion (dry, solid coal), } \% = 1.49\ \text{F.C.} - 11.04 \log \text{Fluidity} - 19.3 \qquad (r = .92)$$

F.C. = fixed carbon, dmmf
Fluidity = Gieseler, maximum dial divs. per min.

For 18 samples of Pocahontas No. 3 coal, these workers found that expansions could be expressed by a linear function of the fixed carbon:

$$\text{Expansion, } \% = 7.3 \times \text{F.C. (dmmf)} - 577 \qquad (r = .95)$$

(Expansion at dry bulk density of 55.5 pcf)

Since straight-line and various types of curvilinear relationships are indicated by the correlations cited, a closer examination of the data is warranted. For the correlation of volume expansion, Bureau of Mines data (for samples from various coal beds) on coal properties and expansion in the sole-heated oven were utilized (Table III).

TABLE III

VOLUME EXPANSIONS IN BUREAU OF MINES SOLE-HEATED OVEN AND ANALYTICAL DATA FOR UNBLENDED COALS

Bur. Mines No.	EXPANDING COALS BED	Expansion % at 55.5 pcf Wet	Volatile Matter (dmmf) CO_2, %	CO_2, %	Mineral Matter, Dry, %	Log of Gieseler Maximum Fluidity	Moisture Total %	Moisture Air-Dry %	Reference Bur. Mines
69	Hartshorne	33.9	15.1	2.53	9.2	- .22	1.6	.5	TP 667
74	"	41.6	14.8	2.08	9.3	- .30	1.6	.7	" 667
70	"	38.8	17.5	1.72	5.7	.58	1.6	.7	" 667
79	"	7.7	22.4	.71	8.1	2.29	3.5	.5	" 667
80	Stigler	17.6	25.6	1.51	5.6	2.57	2.1	.6	" 667
73	McAlester	1.0	37.6	1.49	5.2	.18	3.8	2.7	" 667
62	Powellton	.9	35.3	.01	3.3	3.2	2.5	1.2	" 630
64	Bakerstown	9.8	22.7	.13	6.9	1.93	2.2	.6	" 644
345	Davy Sewell	11.2	20.2	—	8.2	2.61	1.7	.8	IC 7565
332	Sewell (Davy)	12.1	21.1	—	4.8	—	.6	.4	" 7518
55	Sewell	16.0	22.2	.24	3.6	1.95	1.6	.6	TP 601
90	Beckley	15.9	19.9	.52	3.9	2.10	2.3	.5	" 712
282	Poca. No. 3	29.5	16.5	.00	10.4	.15	1.1	.5	" 702
281	" "	28.5	16.6	.00	7.8	.64	1.7	.5	" 702
75	" "	24.4	16.7	.62	6.2	.43	2.4	.5	" 670
56	" "	17.8	18.2	.08	7.5	1.26	1.6	.6	" 604
57	Poca. No. 4	22.5	16.5	.12	8.3	.48	1.4	.4	" 604
280	" "	22.9	16.6	.05	8.1	.69	1.7	.6	" 702
358	" " (1.5 Float)	16.2	18.7	—	6.0	2.15	1.0	.4	IC 7565
333	Poca. No. 6	5.8	18.4	—	8.7	—	1.4	.5	" 7518
347	" "	6.4	18.9	—	8.4	1.79	1.4	.7	" 7565
370	" "	5.7	19.3	—	6.7	3.33	4.4	5	" 7565
89	" "	.2	23.0	.05	15.9	1.10	1.9	.7	TP 711
89a	" " (1.5 Float)	7.8	22.0	.05	9.9	—	.8	.7	" 711
47	Lower Kittanning	43.8	16.9	.04	8.1	.18	1.7	.7	" 595
372	" "	25.1	17.4	—	9.7	.60	2.3	.4	IC 7565
374	" " (Miller)	6.7	23.0	—	8.4	3.20	1.7	.4	" 7565

(TABLE III continued on page 44)

TABLE III (Continued)

VOLUME EXPANSIONS IN BUREAU OF MINES SOLE-HEATED OVEN AND ANALYTICAL DATA FOR UNBLENDED COALS

Bur. Mines No.	BED	Expansion % at 55 S pcf Wet	Volatile Matter (dmmf) CO_2, %	CO_2, %	Mineral Matter, Dry, %	Log of Gieseler Maximum Fluidity	Moisture % Total	Moisture % Air-Dry	Reference Bur. Mines
	EXPANDING COALS								
50	Upper Kittanning	24.2	17.3	.11	11.5	.08	1.8	.4	TP 595
375	" "	18.4	26.5	—	7.1	2.95	1.1	.5	IC 7565
60	Lower Freeport	19.0	26.5	.12	7.5	1.56	2.0	.9	TP 621
87a	Hill	14.8	22.3	—	7.4	1.88	4.7	.8	" 703
87	Hill (washed)	20.3	22.8	—	2.9	1.86	3.1	.9	" 703
	CONTRACTING COALS								
52	Pittsburgh	-15.6	39.7	.22	9.5	2.85	2.4	1.5	TP 594
293	" (washed)	-16.6	37.7	.06	9.0	3.05	3.3*	1.4	" 726
294	"	-15.3	38.6	.23	8.1	3.38	3.1*	1.4	" 726
72	Thick Freeport	- 6.1	37.9	.33	7.7	2.48	2.8	1.5	" 655
291	" "	-12.7	38.6	.24	9.2	4.08	2.4*	1.3	" 726
292	" "	-14.6	38.2	.15	10.6	4.08	2.7*	1.8	" 726
b371	" "	-11.0	37.8	—	8.0	3.74	2.6	1.7	IC 7565
376	Upper Freeport	-11.9	31.7	—	15.6	3.86	.8	.8	" 7565
331	" "	- 7.6	32.2	—	10.6	—	2.0	.9	" 7518
335	" "	-13.5	30.8	—	10.9	—	2.2	.6	" 7518
323	Lower Freeport	- 4.0	31.5	—	9.4	—	2.9	1.1	" 7518
82	Eagle	-21.2	35.1	.09	8.5	4.13	1.6	.9	TP 691
362	"	- 2.6	36.2	—	6.2	3.77	1.9	1.3	IC 7565
86	Elkhorn No. 3	- 1.0	40.3	.17	3.8	2.62	2.9	1.8	TP 697
295	Elkhorn	-11.1	35.9	.01	11.0	2.92	4.0*	1.3	" 726
364	No. 5 Block	-15.9	40.4	—	13.5	1.69	4.9	3.7	IC 7565
88	" "	-17.3	36.5	.05	10.7	4.08	2.0	1.0	TP 711
54	High Splint	- 8.5	39.5	.50	4.6	.78	3.3	2.5	" 599
63	Lower Hignite	- 5.5	39.0	.11	6.0	2.27	2.9	1.4	" 634
61	No. 1	- 2.3	35.5	.05	6.1	2.71	5.4	2.6	" 628
76	Hazard No. 4	- 3.2	39.1	.21	4.6	1.03	3.6	2.4	" 672
77	Hazard No. 7	- 9.5	39.2	.13	7.9	1.11	3.1	2.1	" 672
356	Imboden	- 1.5	38.2	—	5.3	3.27	3.0	1.7	IC 7565
58	Lower Banner	- 6.2	22.6	.29	10.1	2.46	2.5	.5	TP 616
91	" "	-25.8	35.9	1.65	7.3	3.70	1.9	.8	" 720
363	No. 2 Gas	-13.3	38.8	—	6.6	4.48	1.7	.9	IC 7565
366	Stockton-Lewiston	-17.8	42.2	—	14.2	1.99	4.4	2.7	" 7565
83	Powellton	- 9.0	34.1	.16	2.6	3.54	2.2	1.0	TP 691
81	"	- 6.4	33.3	.01	3.7	3.80	2.2	1.0	" 683
53	Pond Creek	- 6.5	33.6	.12	5.2	3.10	2.7	1.1	" 596
312	America (washed)	- 4.3	23.7	.37	11.6	2.73	7.0*	.7	" 726
308	Mary Lee (washed)	- 2.9	30.5	.26	10.8	3.03	5.0*	.6	" 726
309	" "	- 7.3	31.0	.34	11.2	3.11	7.4*	.6	" 726
313	" "	-11.3	33.0	.10	13.2	3.40	6.7*	1.0	" 726
361	Ill. No. 5	- 3.1	38.8	—	9.0	—	6.4	3.1	IC 7565
71	Bevier	-25.1	40.5	1.90	9.9	3.05	4.1	1.9	TP 667
68	Henryetta	- 3.3	37.5	.23	7.4	.40	6.8	4.4	" 667
78	McAlester	- 2.2	35.6	1.96	6.1	2.56	3.0	1.4	" 667
66	No. 5	- 3.5	40.0	.18	7.2	2.47	1.7	1.3	" 649
65	No. 2	- 3.3	31.6	.05	12.9	1.78	2.2	1.2	" 649
426	Sewell	-11.7	30.5	—	6.3	—	2.3	.6	**
429	"	- 4.7	30.8	—	8.5	—	2.4	1.1	**
328A	Palau, Mex.	- 5.6	24.8	—	15.0	—	3.1	—	IC 7518

* Sampled at coke plant

** Report of Gas Prod. Comm., AGA (1950)

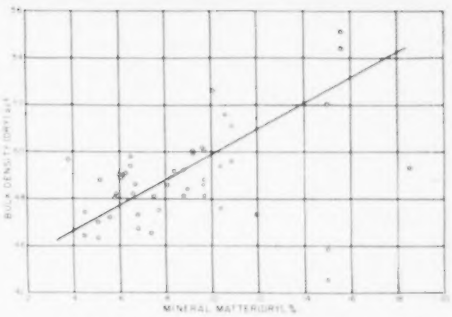

Fig. 28.—Effect of Mineral Matter Upon Bulk Density
(Data from Tables IV and X)

The experimental expansion results are usually calculated to a wet bulk density of 55.5 pcf or to dry, solid-coal expansion, using the expressions given in Appendix V, A, p. 34. However, the authors found that closer correlations were obtained when the experimental results were calculated to a standard dry bulk density corrected to uniform mineral-matter content. In this case, a dry bulk density of 54 pcf at 8% mineral matter was selected as standard, the mineral matter correction being calculated from the slope of the average line shown in Fig. 28. It was also observed that the correlation could be improved by subtracting the CO_2 from the volatile matter, and graphically correcting the percentage expansion for mineral matter (Fig. 29). The arrangement of points for the expanding coals indicates a peak at about 16% volatile matter, corresponding to that noted by Russell (Fig. 27), and also a lesser peak at about 27% volatile matter, in the middle of the medium-volatile range. The contracting coals also show the latter trend, contraction first appearing at 22.5% volatile matter, and not reappearing until 30.5% volatile matter. The almost vertical rise of the lines in the range of 14 to 18% volatile matter shows that expansion is inadequately indicated by volatile matter in this region. The data gave widely-scattered points for coals of more than 31% volatile matter. It will be shown in Appendix VI, B, 3, that properties other than volatile matter must be considered for classification of these high-volatile coals.

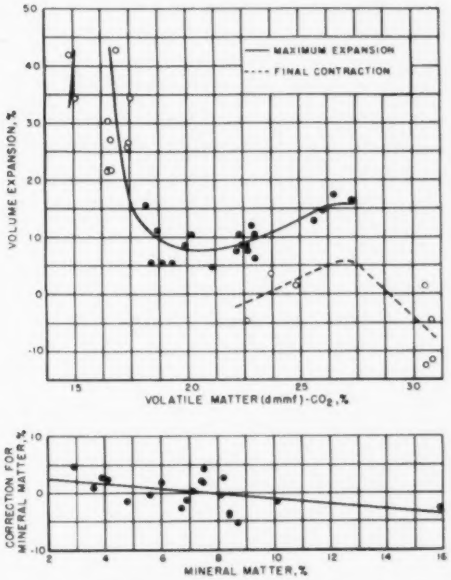

Fig. 29.—Volume Expansion as a Multiple Function of Volatile Matter and Mineral Matter

Note: Test expansions have been calculated to expansion at a standard dry bulk density of 54 pcf at 8% mineral matter. Expansions in the upper graph were corrected to 8% mineral matter by the average line shown in lower graph. Data from Table III.

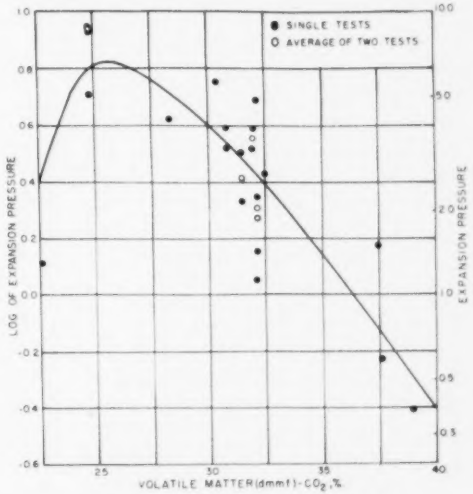

Fig. 30.—Expansion Pressures of Unblended Coals in Bureau of Mines Slot Oven

Note: Expansion pressures have been calculated to a standard dry bulk density of 49 pcf at 8% mineral matter by Fig. 31. Data in Table IV.

TABLE IV

EXPANSION PRESSURES IN BUREAU OF MINES SLOT OVEN AND VARIOUS COAL PROPERTIES FOR UNBLENDED COALS

Bur. Mines No.	BED	Expansion Pressure, psi	Bulk Density, pcf	Moisture % Total	Moisture % Air Dry	Mineral Matter, Dry, %	CO_2, %	Volatile Matter, (dmmf) —CO_2, %	Log of Gieseler Maximum Fluidity	Reference Bur. Mines
331	Upper Freeport	1.5	52.7	2.0	.9	10.6	—	32.2	—	IC 7518
a331	" "	1.1	50.6	3.6	1.1	9.7	—	32.2	—	" 7565
a331	" "	2.0	50.4	3.6	1.1	9.7	—	32.2	—	" 7565
335	" "	3.1	50.8	2.2	.6	10.9	—	30.8	—	" 7518
335	" "	3.7	52.4	2.2	.6	10.9	—	30.8	—	" 7518
376	" "	3.4	55.5	.8	.8	15.6	—	31.5	3.86	" 7565
376	" "	4.3	54.8	.8	.8	15.6	—	31.5	3.86	" 7565
326	Upper and Lower Freeport	1.5	49.4	3.6	1.0	10.4	—	32.2	—	" 7518
326	" "	1.5	51.2	3.6	1.0	10.4	—	32.2	—	" 7518
a326	" "	3.8	49.7	2.7	.8	9.0	—	32.2	—	" 7518
b326	" "	3.6	51.9	3.4	.9	9.8	—	32.0	—	" 7565
b326	" "	4.1	51.7	3.4	.9	9.8	—	32.0	—	" 7565
58	Lower Banner	2.3	53.3	1.3	.5	10.1	.29	22.6	2.46	RI 3644
63	Lower Hignite	0.5	50.0	2.9	1.4	6.0	.11	39.0	2.27	" 3644
68	Henryetta	0.9	49.9	6.8	4.4	7.4	.23	37.5	.40	TP 667
73	McAlester	0.8	50.7	3.8	2.7	5.2	1.49	37.6	.18	" 667
XP36	Mary Lee	2.2	51.8	8.7	.6	11.9	—	30.4	—	RI 4285
235	Rosita, Mexico	1.2	51.5	4.2	—	18.5	—	28.3	—	" 4285
328A	Palau, Mexico	4.2+	53.1	2.0	.7	15.0	—	24.8	—	IC 7518
328A	" "	1.7	48.7	5.9	.7	15.0	—	24.8	—	" 7518
328A	" "	1.3	47.5	6.3	.7	15.0	—	24.8	—	" 7518

The relationship between volatile matter and maximum expansion pressure, as measured in the Bureau of Mines two-wall heated slot oven, is shown in Fig. 30. The test bulk densities (Table IV) were corrected to the dry, 8% mineral matter basis as before. The observed expansion pressures were then calculated to a standard dry bulk density of 49 pcf from the slope of the average line shown in Fig. 12 (p. 34). The experimental error in Fig. 30 is apparently of considerable magnitude, as judged by the deviations between duplicate tests and by the fact that average results deviate less from the average line than single tests. It has been previously mentioned (Appendix IV, A) that the probable error in this apparatus is 0.4 psi.[135] The deviations from the average line in Fig. 30 have been plotted against the bulk density correction line in Fig. 31.

2. Ash or Mineral Matter Content. In Table V are shown the results of several investigations concerning the effect of ash upon maximum ex-

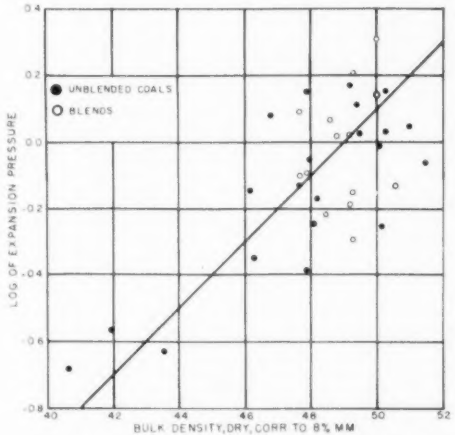

Fig. 31.—Effect of Bulk Density on Expansion Pressure

Note: The points plotted for unblended coals are deviations from the volatile matter correlation curve shown in Fig. 30; those for blends are deviations from the air-dry moisture correlation curve shown in Fig. 36.

pansion pressure.[82] With the exception of one group of data, the higher-ash coals gave lower expansion pressures at test bulk densities. However, when the expansion pressures are converted to a standard bulk density at 8% mineral matter, the results are inconclusive, since the calculated pressures sometimes increase with increases in mineral matter. The inconsistency of results may be due to segregation of petrographic constituents by such operations as washing, hand-picking, or screening.

TABLE V

EFFECT OF ASH CONTENT ON EXPANSION PRESSURE[82]

	Ash in Designated Individual Coal, %	Maximum Expansion Pressure of Blend, psi
Tests Made by C. C. Russell:		
30% Beckley, 70% Elkhorn No. 3:		
Beckley, Clean Seam	4.4	4.37
Beckley, Full Seam	5.2	3.87
Beckley, Slack	10.6	3.50
Tests Made by Inland Steel Co.:		
30% Beckley, 25% Elkhorn No. 3 Egg, 45% Elkhorn No. 3 Egg:		
Beckley, unwashed	10.05	3.2
Beckley, washed at 1.60	8.46	4.2
Beckley, washed at 1.50	5.20	4.2
Beckley, washed at 1.40	4.10	3.6
30% Beckley, 70% Elkhorn No. 3:		
Elkhorn No. 3 Slack	6.8	4.1
Elkhorn No. 3 Egg-Slack	5.4	4.2
Elkhorn No. 3 Egg	3.0	4.6
25% Beckley, 75% Elkhorn No. 3:		
Beckley, raw	—	2.4
Beckley, washed	—	2.9
Normal Properties of Elkhorn No. 3:	**Ash%**	**Max. Exp. Press. psi**
Egg, alone	abt. 2.5	1.67
Slack, alone	abt. 5.5	.91

The correlations of Brown indicated that volume expansion significantly decreased with increasing ash content, when the bulk density was held constant.[35] This effect was probably due to the influence of the mineral matter upon the bulk density. It is shown in the lower part of Fig. 29 that mineral matter exerts a minor influence upon volume expansion, when bulk densities are corrected to uniform mineral matter content. No effect of mineral matter upon expansion pressure was noted for the data plotted in Fig. 30. The rather large corrections for mineral matter found necessary when correlating volume expansion with fluidity

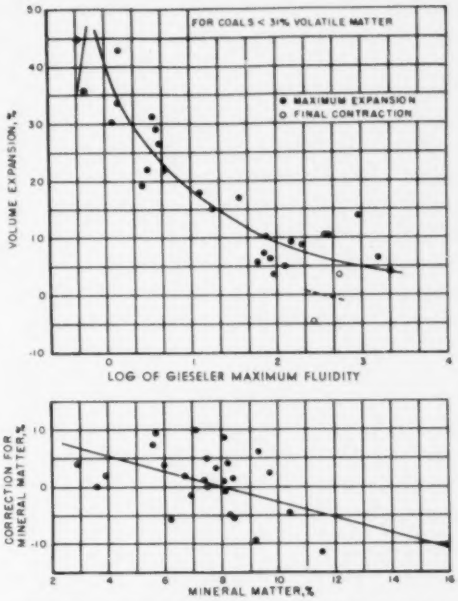
FOR COALS < 31% VOLATILE MATTER
● MAXIMUM EXPANSION
○ FINAL CONTRACTION
VOLUME EXPANSION, %
LOG OF GIESELER MAXIMUM FLUIDITY
CORRECTION FOR MINERAL MATTER, %
MINERAL MATTER, %

Fig. 32.—Volume Expansion as a Multiple Function of Fluidity and Mineral Matter

Note: Test expansions have been calculated to expansion at a standard dry bulk density of 54 pcf at 8% mineral matter. Expansions in the upper graph were corrected to 8% mineral matter by the average line shown in lower graph. Data from Table III.

(Fig. 32) are probably mostly due to the effect of mineral matter upon fluidity.

3. Degree of Oxidation. This may be termed a pseudo-chemical property, since the initial stages of oxidation are not detectable by chemical analysis,[81] although excessive oxidation is characterized by a significant increase in oxygen content.

The effect of oxidation upon the volume expansion of coals has been observed by the Bureau of Mines. Coal samples were subjected to accelerated oxidation by tumbling in a drum in the presence of air at a temperature of 100°F. Sewell coal showed a significant reduction, compared to fresh coal, in linear expansion after 18.8 days of treatment, although no reduction was noted after 5.6 days.[56] In this case, expansion was measured by the extent of deformation of BM-AGA retorts. While no great accuracy is claimed for this method of measurement, it has been shown to qualitatively indicate the expanding properties. Oxidation of

Lower Freeport coal also decreased expansion in proportion to the degree of oxidation.[57]

Representative tests made in the Bureau of Mines sole-heated oven with oxidized coals are shown in Table VI. The expanding properties of the Pocahontas coals were destroyed almost entirely by sufficient oxidation. The Beckley coal showed anomolous behavior in that moderate oxidation increased the expansion. The amount of contraction of the non-expanding Lower Banner coal decreased with time of oxidation.

TABLE VI

EFFECT OF OXIDATION ON VOLUME EXPANSION OF COALS IN BUREAU OF MINES SOLE-HEATED OVEN

	Oxidation, Days	Expansion, %
Pocahontas No. 4[45]	0	22.9
	2.7	22.7
	7.5	6.2
	11.9	- 1.5
Pocahontas No. 3[45]	0	28.5
	3.7	20.4
	8.3	2.6
	11.5	.9
Beckley[52a]	0	15.9
	8.2	30.0
	18.4	3.6
Lower Banner[46]	0	-25.8
	3.9	-17.8
	11.2	-16.9
	19.2	-16.1

The limited data available indicate that expansion pressures are reduced by the inclusion of oxidized coals in the blend. One test showed that the maximum expansion pressure of a blend was decreased from 6.1 psi for fresh coal to 0.8 psi for the same blend oxidized for 19 hours at 150° C. in air. Outcrop or oxidized low-volatile coals (as indicated by small, weak volatile-matter buttons) gave maximum expansion pressures of 1.6 psi in blends with a standard high-volatile coal, compared to about 3.5 psi for fresh low-volatile coals blended in the same manner. Since Savage[174] has shown that a certain percentage of oxidized coals may be used in a blend without any deleterious effect upon the coke quality, it is probable that small proportions of oxidized coal will not affect expansion pressure.

These effects of oxidation upon expansion may be reconciled by consideration of the effects of oxygen upon the coal. The decreased fluidity[167] accompanying oxidation is probably due to alteration of the chemical structure by removal of hydrogen and addition of oxygen; if the plastic layer is continuous, the decreased fluidity would tend to increase expansion. However, excessive oxidation reduces swelling, an effect which has been frequently observed in the free-swelling index and appearance of the volatile-matter button. Recent evidence indicates that this decrease in swelling is due to the opening of the capillary structure by oxidation.[19] Sufficient decreases in swelling would, of course, lead to more permeable plastic envelopes and reduced exansion pressures.

B. Physical Tests

1. Fluidity. The Pontypridd Test Plant Committee found a rather poor correlation between Gieseler maximum fluidities and expansion in a modified Russell oven.[111] For some seventy English coals, a correlation coefficient of only 0.53 was obtained.

Reference has been made (Fig. 1) to the somewhat closer relationship presented by Russell and Perch between the Gieseler fluidities and expansion pressures of American coals.[167]

An inverse relationship between Gieseler maximum fluidity and volume expansion measured in the Bureau of Mines sole-heated oven is indicated by the multiple linear correlations given in Appendix VI, A, 1.

Since the references cited are somewhat contradictory, recourse was made to correlation of the data in Table III to obtain a clearer view of the role of fluidity in volume expansion. Plotting of the data (Fig. 32) indicated a mineral-matter correction greater than required in the volatile-matter correlation (Fig. 29). It has been mentioned that this larger correction is probably due to the effect of mineral matter in decreasing the fluidity. No relationship between Gieseler maximum fluidity and volume expansion for coals of more than 31% volatile matter was found. The general similarity of the average curve for volume expansion to that for expansion pressure (Fig. 27) is a strong indication that a relationship exists between these two properties in the range of 14 to 31% volatile matter.

Unfortunately, only a few comparable sets of data on fluidities and expansion pressures in the Bureau of Mines slot oven (Table IV) have been published.

2. Other Plasticity and Swelling Tests. Besides the fluidity methods, mention should be made of a number of miscellaneous tests which have been

used in coal testing. Although negative results have been obtained in the application of most of these methods to coal expansion, some have been found to provide information concerning low-rank and oxidized coals.

It is perhaps unnecessary to point out that the free-swelling index bears no direct relationship to coal expansion.[178,4] This index has been correlated with carbon and hydrogen contents by Mott,[125] and has been shown to be affected by oxidation, inert content, petrographic composition, and degree of compaction.[19, 125, 126, 153, 183]

The agglutinating index has also been correlated with the carbon and hydrogen contents by Mott.[129] This test has been recommended as the best indication of degree of oxidation by Schmidt.[176] Weed has shown the application of this test to the selection and blending of coals oxidized in storage, where coke quality was the main consideration.[200]

The volume of the button obtained in the volatile-matter test has also been used as an indication of the extent of oxidation.[200]

Some attempts have been made to relate the results of laboratory swelling tests with those of pilot ovens. McCartney and Davis compared results of the Agde-Damm dilatometer test with volume expansions in the Bureau of Mines sole-heated oven; no relationship was noted, and the dilatometer test was subsequently discontinued by the Bureau.[105] The Pontypridd Test Plant Committee also found little relationship between results from the H. Koppers and Nedelmann (laboratory swelling) tests and the expansion pressures of the same coals in its modified Russell oven.[144] It may be concluded that laboratory swelling tests do not furnish any direct indication of the expansion behavior in large-scale tests.

3. Differences in Ultra-Fine Structure. The significance of the physical structure of coals may be judged from the importance assigned to the natural (bed) moisture in coal classification and correlation studies. The ASTM Classification of Coals by Rank (D388-38) classifies coals of less than 69% fixed carbon (dmmf) according to *moist* mineral-matter-free Btu.[10] The natural bed moisture is specified, the sample to be free of visible surface moisture, if possible. If surface moisture is visible, it is required that the sample be equilibrated at 30°C. and 97% humidity before the determination of total moisture.

Perch and Russell have proposed the classification of coals by the sum of the volatile matter and total moisture.[141] This abscissa appears to satisfactorily classify coals of more than 25% volatile matter, when plotted against the ratio of the moist mineral-matter-free Btu to the dry mineral-matter-free volatile matter. Between 20 and 35% volatile matter, the inclusion of the moisture resulted in no improvement over the use of volatile matter alone; below 20% volatile matter, the spread of points was greater than that obtained with volatile matter alone.

South Metropolitan Gas Co. has used moisture at 50% humidity and volatile matter for classifying coals.[186]

Berkowitz utilized the moisture content of the air-dried sample and the volatile matter in joint correlation of the coking properties of English and Commonwealth coals.[20] The coking properties correlated were the agglutinating value and free-swelling index.

Despite the obvious importance of physical structure, there is little data available on American coals. Limited studies of the moisture sorption of several coals have confirmed the existence of a capillary type of structure.[70, 146, 152] Heats of wetting, principally with water, were determined for a few coals by Porter and Ralston.[146] However, there is no data available for correlation with expansion behavior except that which may be deduced from the total and air-dried moisture contents. From the data given in Appendix **II**, C, p. 21, these measures should furnish approximate indication of relative porosities and total surface areas.

The significance of moisture to the volume expansion of unblended coals was ascertained from the data given in Table III. There is a reasonable correlation between the total and air-dry moistures of these samples (Fig. 33), with the exception of a group of coals whose total moistures appeared to be unusually high. It is possible that these high moistures were due to surface moisture on the coal. The air-dry moisture was therefore selected as the more reliable indication of physical structure. This selection permitted the inclusion of coals sampled at the point of delivery and also of washed coals, the total moistures of which would probably deviate from the bed moistures.

No significant influence of air-dry moisture upon expansion was noted for coals of less than 30 to 35% volatile matter. Of the coals shown in Table III, all of those expanding more than 1%

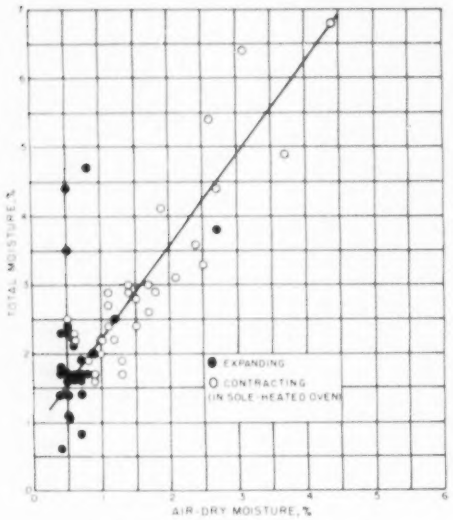

Fig. 33.—Relationship Between Air-Dry and Total Moisture

had substantially the same air-dry moisture, 0.65 ± 0.25%. However, the air-dry moisture was found to be significant in multiple correlation of the volume expansions of coals with volatile matter contents exceeding 31%. (Fig. 34). It may be noted that these expansions could not be successfully correlated with either volatile matter or fluidity or a combination of the two.

Expansion pressure data are available for too few unblended coals in the high-volatile range for multiple correlation with air-dry moisture (Table IV). However, it will be shown in a subsequent section on coal blends that the air-dry moisture of the high-volatile coal was the most significant variable which could be related to the expansion behavior.

The dependence of expansion upon air-dry moisture is rather remarkable in view of the lack of precision which is an inherent defect of air-dry moisture determinations. Bond has shown that the air-dry moisture is dependent upon such variables as ambient temperature and humidity, and particle size.[28]

4. Petrographic Composition and Inert Content. Several investigators have undertaken laboratory carbonization of petrographic fractions, to deter-

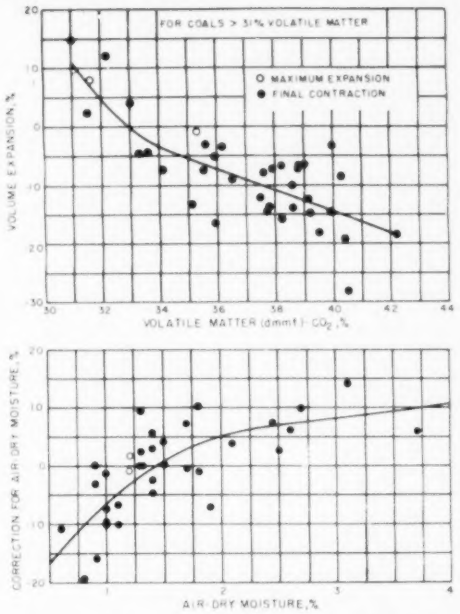
FOR COALS > 31% VOLATILE MATTER
O MAXIMUM EXPANSION
● FINAL CONTRACTION
VOLUME EXPANSION, %
VOLATILE MATTER (dmmf) - CO_2, %
CORRECTION FOR AIR-DRY MOISTURE, %
AIR-DRY MOISTURE, %

Fig. 34.—Volume Expansion as a Multiple Function of Volatile Matter and Air-Dry Moisture

Note: Test expansions have been calculated to expansion at a standard dry bulk density of 54 pcf at 8% mineral matter. Expansions in the upper graph were corrected to 1.4% air-dry moisture by the average line shown in lower graph. Data from Table III.

mine differences in their swelling behaviors.

Mainz and Schwarzmann investigated the effect of petrographic composition upon the expansion of German coals and coal fractions in the Koppers laboratory apparatus.[123] For three seams, the hand-picked bright fractions (mainly vitrain and clarain) expanded much more than the dull fractions (mainly durain and fusain). It was concluded that from 10 to 15% of durain in the mix would eliminate swelling.

Ussar used the laboratory apparatus of Imhof for the investigation of Saar and Ruhr coals.[199] The bright coal (vitrain and clarain) exerted a greater pressure than either the dull coal (durain and fusain) or fiber coal (fusain and vitro-fusain).

Seventeen bright fractions from American (Appalachian) coals gave more swollen and cellular low-temperature coke residues than were obtained from the splint fractions.[188] The differences be-

TABLE VII

PETROGRAPHIC COMPOSITION OF COALS TESTED FOR EXPANSION BY BUREAU OF MINES

Coal No.	TYPES: Bright	Semi-Splint	Splint	COMPONENTS: Anthraxylon	Translucent Attritus	Opaque Attritus	Fusain
Expanding							
74	98	2	0	72	17	6	5
73	100	0	0	76	17	4	3
62	74	17	9	51	30	15	4
64	91	3	6	67	21	10	2
55	81	15	4	60	23	12	5
56	88	2	10	60	20	11	9
57	90	5	*	57	30	11	2
47	100	0	0	88	24	7	1
50	100	0	0	66	18	13	3
60	93	5	2	68	24	7	1
			*5% Cannel				
Contracting							
52	86	12	2	64	21	12	3
72	96	4	0	61	28	8	3
82	—	—	—	37	39	19	5
54	33	14	53	31	41	26	2
63	75	2	23	51	32	15	2
61	91	3	6	54	26	13	7
76	—	—	—	55	31	11	3
71	100	0	0	88	22	6	4
68	100	0	0	74	17	4	5
66	100	0	0	67	32	1	tr.
65	100	0	0	75	23	2	tr.
58	36	53	**	30	49	19	2
53	69	18	13	43	37	16	2
			** 11% Cannel				

Note: Other data and literature references for these coals are given in Table III.

tween bright and splint buttons were very marked for the high-rank coals, and less noticeable for low-rank coals.

In addition, vitrain and clarain showed greater swelling than durain and fusain in the standard free-swelling test.[151]

Although carefully selected coal fractions differ in expansion behavior, the influence of petrographic composition is obscure when naturally-occurring full-seam samples are considered. The available petrographic compositions of the coals used in the correlations prepared for this report are given in Table VII. Since the range of petrographic composition is rather narrow, all but three of the coals being predominantly bright, it was found that with these data no quantitative influences upon expansion could be assigned to petrographic composition.

The effect upon expansion of the addition of inert materials to the charge has also been observed. Tests in the Brown oven showed that the volume expansion of Upper Freeport coal was lowered from an initial value of 5.5% to 1.1% by increasing the fusain content from 3.9% to 12.7%.[35] The differences in expansion of the two samples could be accounted for by calculating the dry, solid-coal expansion.[12] Table VIII shows the reduction in expansion pressure in the Russell oven caused by the addition of inert materials to low-volatile coals. Anthracite fines and low-temperature coke gave reductions in expansion pressure without significantly affecting the bulk density of the charge. Sawdust additions resulted in a considerable decrease in bulk density. H. Koppers also showed that the addition of 10% of finely ground coke breeze lowered expansion pressure from 9.1 down to 6.0 psi.[59]

TABLE VIII

EFFECT OF INERTS ON MAXIMUM EXPANSION PRESSURE[168]

	Bulk Density, pcf	Max. Expansion Press., psi
Mixtures with Pocahontas No. 3:		
Anthracite Fines, 0%	51.0	4.3
" " 2%	51.2	3.75
" " 5%	51.0	2.75
" " 8%	52.3	1.2
Low-Temp. Coke, 0%	51.0	4.3
" " " 5%	50.9	2.6
" " " 8%	49.6	2.0
Beckley and Sawdust Mixtures:		
Sawdust, 0%	49.7	9.9
" 4%	46.2	5.9
" 6%	44.4	1.3
" 8%	41.3	.8

C. Coal Mixtures

Since 85% of the coal carbonized is charged as blends, usually of high- and low-volatile coals, the work which has been done on coal blends, although more limited in scope than the work referred to on unblended coals, is of considerable practical importance.

Early work on the volume expansion of binary blends of high- and low-volatile coals indicated that the expansion of a blend could be approximated by calculating the weighted average of the expansions of the constituent coals.[55]. The later examination of a large number of blends by Nau-

gle, however, showed a consistent deviation from the weighted average. The following expressions were found to approximate the expansions of blends containing 20 and 30% low-volatile coal:[135]

20% Low-Volatile: $E_B = .600\ (.20\ E_{LV} + .80\ E_{HV}) + 21.4$ (30 tests) $(r = .89)$

30% Low-Volatile: $E_B = .477\ (.30\ E_{LV} + .70\ E_{HV}) + 28.5$ (23 tests) $(r = .85)$

E = dry, solid coal expansion, %
B, LV, and HV refer to blend, low-volatile and high-volatile, respectively.

These equations were obviously based upon the assumption that both the high- and low-volatile coals contributed to the expansions of blends. To detect the relative influences of the two different kinds of coal, the authors examined the data shown in Table IX. Correlation failed to reveal any influence of the low-volatile coal, and showed that the expansion of blends in this range of composition may be expressed as simple equations involving only the expansion of the high-volatile coal:

20% Low-Volatile: $E_B = .728\ E_{HV} + 6.4$ (26 tests) $(r = .91)$

30% Low-Volatile: $E_B = .576\ E_{HV} + 7.1$ (15 tests)

E = expansion at wet bulk density of 55.5 pcf, %
B and HV refer to blend and high-volatile, respectively.

The average deviation of the observed results from those calculated by the equations is 1.7% in each case.

The expansion pressures of binary blends of high- and low-volatile coals are shown in Fig. 35. It will be noted that the relationship is not straight-line, and that the inflection points occur at different percentages for the various blends.

Expansion pressures in the Bureau of Mines slot oven and selected coal properties of blends containing from 17.5 to 30% low-volatile coal are shown in Table X. The only significant variable which could be identified was the air-dry moisture of the high-volatile coal. The expansion pressures, corrected to standard bulk density at 8% mineral matter, are shown plotted against the air-dry moisture in Fig. 36, with the deviations plotted against

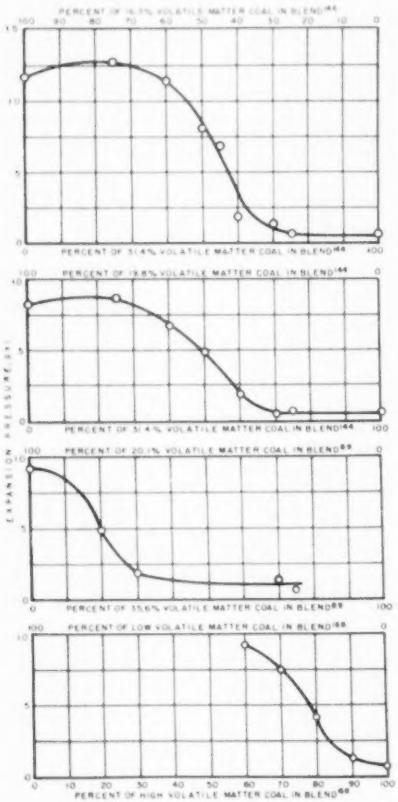

Fig. 35.—Effect of Blending on Expansion Pressure

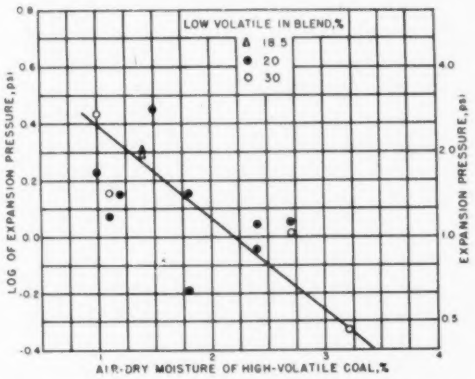

Fig. 36.—Expansion Pressures of Coal Blends vs. Air-Dry Moistures of the High-Volatile Coal

Note: Test pressures have been converted to pressures at a standard dry bulk density of 49 pcf at 8% mineral matter (see Fig. 31). Data from Table X.

TABLE IX

EXPANSION OF BLENDS IN BUREAU OF MINES SOLE-HEATED OVEN

BLEND		LOW VOLATILE COAL			HIGH VOLATILE COAL			
Coal No.	Expansion, %	Coal No.	Bed	Expansion, %	Coal No.	Bed	Expansion, %	Reference Bur. Mines
20% Low-Volatile Mixtures								
72C	5.0	56	Poca. No. 3	17.8	72	Th. Freeport	- 6.1	TP 655
76A	3.1	75	" " "	(24.4)	76	Hazard No. 4	- 3.2	" 672
81A	3.2	75	" " "	(24.4)	81	Powellton	- 6.4	" 683
82A	-11.8	75	" " "	(24.4)	82	Eagle	-21.2	" 691
86A	5.1	75	" " "	(24.4)	86	Elkhorn No. 3	- 1.0	" 697
91A	-11.5	75	" " "	(24.4)	91	Low. Banner	-25.8	" 720
93A	- 7.9	75	" " "	(24.4)	93	Chilton	-20.3	IC 7518
94A	- 4.0	75	" " "	(24.4)	94	Low. Cedar Grove	-11.3	" 7518
322A	- 6.3	75	" " "	(24.4)	322	Elkhorn No. 3	- 9.5	" 7518
356A	6.5	75	" " "	(24.4)	356	Imboden	- 1.5	IC 7565
361A	1.3	75	" " "	(24.4)	361	Illinois No. 5	- 3.1	" 7565
362D	5.1	357	" " "	10.9	362	Eagle	- 2.6	" 7565
363A	0.7	357	" " "	10.9	363	No. 2 Gas	-13.3	" 7565
347A	- 4.8	347	Poca. No. 6	6.4	28	Pittsburgh	(-14.0)	" 7565
370A	- 4.0	370	" " "	5.7	28	"	(-14.0)	" 7565
b371A	1.0	372	Low. Kittanning	25.1	b371	Th. Freeport	-11.0	IC 7565
c371A	6.5	372	" "	25.1	c371	" "	- 4.4	" 7565
d371A	- 0.2	372	" "	25.1	d371	" "	- 9.9	" 7565
e371A	- 3.6	372	" "	25.1	e371	" "	-15.1	" 7565
f371A	- 3.3	372	" "	25.1	f371	" "	-11.2	" 7565
374A	- 4.3	374	" "	6.7	28	Pittsburgh	(-14.0)	" 7565
375A	- 5.6	375	Up. Kittanning	18.4	28	"	(-14.0)	" 7565
73A	5.7	74	Hartshorne	41.6	73	McAlester	1.0	TP 667
87A	- 1.5	87	Hill	20.3	28	Pittsburgh	(-14.0)	" 703
90A	- 3.6	90	Beckley	15.9	28	"	(-14.0)	" 712
345A	- 3.7	345	Davy Sewell	11.2	28	"	(-14.0)	IC 7565
30% Low-Volatile Mixtures								
76B	4.9	75	Poca. No. 3	(24.4)	76	Hazard No. 4	- 3.2	TP 672
81B	5.1	75	" " "	(24.4)	81	Powellton	- 6.4	" 683
82B	-5.9	75	" " "	(24.4)	82	Eagle	-21.2	" 691
86B	4.3	75	" " "	(24.4)	86	Elkhorn No. 3	- 1.0	" 697
91B	-6.0	75	" " "	(24.4)	91	Low. Banner	-25.8	" 720
93B	-4.3	75	" " "	(24.4)	93	Chilton	-20.3	IC 7518
94B	-0.5	75	" " "	(24.4)	94	Low. Cedar Grove	-11.3	" 7518
322B	-3.5	75	" " "	(24.4)	322	Up. Elkhorn	- 9.5	" 7518
356B	8.3	75	" " "	(24.4)	356	Imboden	- 1.5	IC 7565
361B	3.2	75	" " "	(24.4)	361	Illinois No. 5	- 3.1	" 7565
291B	1.5	—	" " "	(24.4)	291	Th. Freeport	-12.7	TP 726
374B	-0.7	374	Low. Kittanning	6.7	28	Pittsburgh	(-14.0)	IC 7565
375B	* -2.0	375	Up. Kittanning	18.4	28	"	(-14.0)	" 7565
73B	5.2	74	Hartshorne	41.6	73	McAlester	1.0	TP 667
90B	1.0	90	Beckley	15.9	28	Pittsburgh	(-14.0)	" 712

the bulk density (corrected to 8% mineral matter) in Fig. 31.

Russell has shown that the expansion pressures of some binary blends varied inversely with the blend fluidities.[168] Apparently, the relationship is not generally applicable, since Isenberg's results indicate that expansion pressure may be lowered by substitution of a coal of either high or low fluidity for one of moderate fluidity.[82] With a blend of 30% Beckley, 45% Elkhorn No. 3 Slack, and 25% Elkhorn Egg, the mixture developing 4.2 psi pressure, substitution of highly fluid Eagle coal for the Elkhorn Egg reduced the pressure to 3.0 psi. Substitution of Illinois No. 6, a coal of low fluidity, likewise reduced the expansion pressure, in this case to 2.6 psi.

TABLE X

EXPANSION PRESSURES OF BLENDED COALS IN BUREAU OF MINES SLOT OVEN

Coal Mix No	COAL AND PROPORTION IN MIX	BLENDED COALS: Expansion Pressure, psi	BLENDED COALS: Bulk Density, pcf	BLENDED COALS: Total Moist., %	BLENDED COALS: Mineral Matter, dry, %	SEPARATE COALS: Air Dry Moist., %	SEPARATE COALS: Volatile Matter (dmmf) CO_2, %	SEPARATE COALS: Log of Gieseler Maximum Fluidity	Reference Bur Mines
b72A	20% Low Kittanning	1.5	51.5	2.6	9.4	—	—	—	TP 655
	80% Thick Freeport (1" sl.)					1.2	37.4	—	
72C	20% Pocahontas No. 3	2.1	48.8	(2.6)	(7.7)	0.6	18.2	1.26	" 655
	80% Thick Freeport					1.5	37.9	2.48	
73A	20% Hartshorne	1.4	50.8	3.5	6.2	.7	14.8	-.30	" 677
	80% McAlester					2.7	37.6	.18	
73B	30% Hartshorne	1.1	50.3	3.3	6.7	.7	14.8	-.30	" 677
	70% McAlester					2.7	37.6	.18	
XP56A	20% Pocahontas No. 3	1.5	49.8	2.5	8.1	.6	18.2	1.26	RI 4285
	80% Pittsburgh					(1.0)	(38.5)	(2.99)	
90B	30% Beckley	3.4	49.9	1.7	6.3	.5	19.9	2.10	IC 7417
	70% Pittsburgh					1.0	38.5	2.99	
76A	20% Pocahontas No. 3	0.7	47.9	3.3	5.1	.5	16.7	.43	TP 672
	80% Hazard No. 4					2.4	39.0	1.03	
76B	30% Pocahontas No. 3	1.0	48.6	3.2	5.1	.5	16.7	.43	" 672
	70% Hazard No. 4					2.4	39.0	1.03	
81A	20% Pocahontas No 3	2.2	50.7	2.0	3.8	.5	16.7	.43	" 683
	80% Powellton					1.0	33.3	3.80	
82D	30% Pocahontas No. 3	1.5	49.0	1.9	(5.8)	.5	16.7	.43	RI 4285
	70% Eagle and Powellton					1.1	34.1	3.73	
86B	30% Pocahontas No. 3	1.2	47.7	(2.8)	(4.5)	.5	16.7	.43	TP 697
a86B	70% Elkhorn No. 3	0.7	48.8	(2.8)	(4.5)	1.8	(40.3)	2.62	" 697
87A	20% Hill	1.7	50.7	1.8	6.5	.9	22.8	1.86	" 703
	80% Pittsburgh					1.1	38.3	2.99	
322A	20% Pocahontas No. 3	0.5	49.8	3.9	5.8	.5	16.7	.43	IC 7518
	80% Upper Elkhorn No. 3					3.2	40.8	(2.62)	
322B	30% Pocahontas No. 3	0.5	50.1	3.7	5.9	.5	16.7	.43	" 7518
	70% Upper Elkhorn No. 3					3.2	40.8	(2.62)	
d371A	17.5% Lower Kittanning	1.5	49.7	3.3	8.8	.4	17.4	.60	" 7565
	82.5% Thick Freeport	1.9	50.9	3.4	8.8	1.4	38.5	3.46-3.74	" 7565

DEFINITIONS AND ABBREVIATIONS

Since no strict nomenclature has been established in this field of investigation, definitions of terms will be helpful. These definitions are not intended to be comprehensive, but indicate the meanings in which the terms were used in this report:

Coke: the coherent, cellular residue from the destructive distillation of certain bituminous coals (as defined by Rose[16a]).

Expansion Pressure: the force (pressure per unit area) exerted by a charge during carbonization. This pressure is usually measured in a slot-type, two-wall-heated oven.

Volume Expansion (Linear or Percentage Expansion, Final Contraction): the volume change occurring during carbonization, usually expressed as a percentage of the charge dimension perpendicular to the heating surface. This expansion is ordinarily measured in a sole-heated oven under the load of a movable piston on the side opposite the heating surface.

Coal Rank: the basis of the ASTM Classification of Coals by Rank[19] is the proximate analysis and heating value. Condensed specifications are as follows (all on the mineral-matter free basis):

Coal Class and Group	Dry Fixed Carbon, %	Moist Btu
I Anthracitic	86% or more	
II Bituminous		
1. Low volatile	78-86	
2. Medium volatile	69-78	
3. High volatile A	less than 69%	14,000 or more
4. High volatile B	less than 69%	13,000-14,000
5. High volatile C	less than 69%	11,000-13,000
III Sub-bituminous	less than 69%	8,300-11,000
IV Lignitic	less than 69%	less than 8,300

Free Swelling: volume expansion with no load on the charge.

Plasticity: that property of a body by virtue of which it tends to retain its deformation after reduction of the deforming stress to its yield stress.[29]

Fluidity: plasticity as measured by torsional tests. In the case of the Gieseler apparatus, fluidity is expressed in dial divisions per minute.

Permeability: the relationship between the pressure-drop and the resulting rate of flow of gas through a plastic medium.

Total Moisture: water as determined by drying at 105° C. For samples from freshly-exposed mine faces, this figure approximates the bed moisture.

Air-Dry Moisture: water retained by the air-dried sample. If expressed as a percentage of the as-received sample, the air-dry moisture equals total moisture minus air-drying loss.

ABBREVIATIONS

A	Angstrom unit, 10^{-8} cm.
daf	dry, ash-free
dmmf	dry, mineral-matter free
F.C.	fixed carbon
psi	pounds per square inch
pcf	pounds per cubic foot
r	correlation coefficient (1.0 = perfect correlation, 0 = no correlation)
V.M.	volatile matter

SELECTED BIBLIOGRAPHY

1 van Ackeren, J. "Improvements in and Relating to the Automatic Control of the Bulk Density of Particulate Coal." Brit. Pat. 620,133 (1949); U.S. Pat. 2,510,158 (1950).

2 Agroskin, A. A. "Distribution of Pressure in the Chamber of the Coke Oven." *Coke and Chem.* (USSR), No. 3, 34-38 (1939).

3 Agroskin, A. A., and Luskutova, E. N. "Use of Solid Additions to Increase the Pour Weight of Coal." *Bull. acad. sci. URSS, Classe sci. tech.*, 147-156 (1946); *Chem. Abs.*, **40**, 4865 (1946).

4 Agroskin, A. A., and Zagrebel'naya, V. S. "The Theory of Wetting the Coal Charge with Small Quantities of Hydrocarbon Liquids." *Ibid.*, 190-202 (1945); *Chem. Abs.*, **10**, 2283 (1946).

5 ——— "Changes in the Bulk Density of Coal Due to Freezing." *Ibid.*, 83-92 (1947); *Chem. Abs.*, **41**, 5282 (1947).

6 Altieri, V. J. "Measurement of the Expansion of Coal During Carbonization." *AGA Proc.*, 812-836 (1935); *Amer. Gas J.*, **143**, 43, Nov. (1935).

7 —— "Stresses and Strains Generated During Carbonization." *AGA Proc.*, 635-656 (1940).

8 American Coke and Coal Chemicals Institute, Coal and Coke Research Committee. "Coal Blending with Inerts." May 24, 1948.

9 Arthur, J. R., and Wadsworth, K. D. "The Effect of Inorganic Compounds on the Behavior of Coals and Cokes." *BCURA Bull.*, **8**, 296-304 (1944).

10 ASTM Committee D-5. "ASTM Standards on Coal and Coke." Am. Soc. Testing Matls. (1948).

11 Auvil, H. S., and Davis, J. D. "Determination of the Swelling Properties of Coal During the Coking Process." Bur. of Mines RI 3403 (1938).

12 Auvil, H. S., Davis, J. D., and McCartney, J. T. "Expansion of Coal During Coking." Bur. of Mines RI 3451 (1939).

13 ——— "Shrinkage of Coke." Bur. of Mines RI 3539 (1940).

14 Auvil, H. S., Schmidt, L. D., and Graham, H. G. "Control of Bulk Densities in Coke Ovens: Studies on Precision and Application of Various Testing Methods." Bur. of Mines RI 3935 (1946).

15 Bangham, D. H., Franklin, R. E., Hirst, W., and Maggs, F. A. P. "A Structural Model for Coal Substance." *Fuel*, **28**, 231-238 (1949).

16 Barritt, D. T. "Practical Experience in the Coking of Dangerous Low-Ash Coals." *J. Inst. Fuel*, **20**, 161-179, 185 (1947).

17 Becker, J. "Coking Chamber with Enlarged Upper Portion." U.S. Pat. 2,447,837 (1948).

18 Bennett, J. G. "Broken Coal." *J. Inst. Fuel*, **10**, 22-29 (1936).

19 Berkowitz, N. "A Physical Approach to the Theory of Coking." *Fuel*, **28**, 97-102 (1949).

20 —— "The Distribution of Coking Properties in British and Commonwealth Coals." *Ibid.*, **29**, 138-143 (1950).

21 Biddulph-Smith, T. "Notes on the Mechanism of the Carbonization Process, with Special Reference to the Formation and Prevention of Coke Sponge." *Gas World*, **113** (Coking Sect.), 62-67 (1940).

22 —— "Coke Sponge and the Flow of Gases in the Coke Oven." *Ibid.*, **116** (Coking Sect.), 9-10 (1942).

23 —— "The Physical and Chemical Reactions of Carbonization." *Gas J.*, **246**, 56, 59-60, 65-66, 69 (1945).

24 Blayden, H. E., Riley, H. L., and Shaw, F. "The Agglutination and Swelling of Coking Coal." *Fuel*, **25**, 13-24 (1946).

25 Blayden, H. E., Gibson, J., and Riley, H. L. "A Study of Bituminous Coal by Exhaustive Solvent Extraction and X-Ray Diffraction." *J. Chem. Soc.*, 1693-1700 (1948).

26 Bond, R. L., and Maggs, F. A. P. "New Basis for Measurement of Specific Surface of Carbonaceous Powders." *Fuel*, **28**, 169-171 (1949).

27 ——— "Particle Size and Pore Structure of Finely-Ground Coal Chars." *Ibid.*, **28**, 172-175 (1949).

28 Bond, R. L., Griffith, M., and Maggs, F. A. P. "Water in Coal." *Ibid.*, **29**, 83-93 (1950).

29 Brewer, R. E. "Plastic and Swelling Properties of Bituminous Coking Coals." Bur. of Mines Bull. 445 (1942).

30 —— "Plastic Characteristics of Coal." *Ind. Eng. Chem.*, **36**, 1165-1168 (1944).

31 Brewer, R. E., Holmes, C. R., and Davis, J. D. "Plastic Properties of Bituminous Coking Coals. Effect of Petrographic Composition." *Ibid.*, **32**, 792-797 (1940).

31a ——— "Plastic Properties of Bituminous Coking Coals. Effect of Oxidation." *Ibid.*, **32**, 930-934 (1940).

32 Brewer, R. E., et. al. "Carbonizing Properties of Coking Coals." *Ibid.*, **40**, 1243-1254 (1948).

33 Brough, J. R. "Certain Factors Affecting the Bulk Density of Coal." Master's Thesis, Inst. of Gas Tech. (1949).

34 Brown, W. T. "Plan to Improve Blast Furnace Coke." *Bl. Furn. Steel Plant*, **30**, 1137-1145, 1255-1263 (1942).

35 —— "Coal Expansion." *AGA Proc.* 640-679 (1938); *Bl. Furn. Steel Plant*, **27**, 172-174 (1939).

36 Brückner, H. "Investigation Procedures for Solid Fuels." (R. Oldenbourg, 1943).

37 Cady, G. H. "Modern Concepts of the Physical Constitution of Coal." *J. Geol.*, **50**, 337-356 (1942).

38 Cannon, C. G., and Sutherland, G. B. "Infra-Red Absorption Spectra of Coals and Coal Extracts." *Trans. Far. Soc.*, **41**, 279-288 (1945).

39 Cannon, C. G., Griffith M., and Hirst, W. "The Carbonization of Coals." Ultrafine Structure of Coals and Cokes (BCURA, 1944).

40 Cook, R. H. "A Study of Certain Factors Affecting the Bulk Density of Coal." Master's Thesis, Inst. of Gas Tech. (1948).

41 Damm, P., and Korten, F. "The Path of Gases in a Coke Oven." *Gluckauf*, **67**, 1339-1345 (1931); *Chem. Abs.*, **26**, 1754 (1932).

42 Davies, R. G., and Mott, R. A. "Studies in Coke Formation." *Fuel*, **12**, 294-303, 330-340, 371-382 (1933).

43 Davis, J. D. "Selection of Coals for Coke Making." Bur. of Mines RI 3601 (1942).

44 Davis, J. D., and Reynolds, D. A. "Survey of Carbonizing Properties of American Coals." Report of Gas Prod. Comm., AGA, 47-58 (1949).

45 Davis, J. D., et. al., Bur. of Mines TP 702 (1947).

46 ——— Bur. of Mines TP 720 (1949).

47 Dresel, E. M., and Griffith, M. "The Significance of the Heats of Wetting of Coal Powders Ground to Various Degrees of Fineness." *Fuel*, **28**, 193-199 (1949).

48 Dryden, I. G. C. "The Behavior of Bituminous Coals Towards Solvents." *BCURA Bull.*, **13**, 113-138 (1949).

49 Edwards, A. H. "Analysis and Testing of Solid Fuel. Part III. Carbonization, Petrology, Reactivity, etc." *Ibid.*, **12**, 353-363 (1948).

50 Erkin, L. I. "Determination of Lateral Contraction of Coke Mass in Coking Process." *Zavodskaya Lab.*, **14**, 1224-1229 (1948).

51 Erkin, L. I., and Petrov, V. K. "A New Apparatus for the Measurement of Vertical Settling of the Coking Mixture." *Ibid.*, **12**, 88-92 (1946).

52 Fieldner, A. C., and Ambrose, P. M. "Annual Report of Research and Technologic Work on Coal, Fiscal Year 1947." Bur. of Mines IC 7446 (1948).

52a ——— "Annual Report of Research and Technologic Work on Coal, Fiscal Year 1946." Bur. of Mines IC 7417 (1947).

53 Fieldner, A. C., and Gottlieb, S. "Annual Report of Research and Technologic Work on Coal, Fiscal Year 1948." Bur. of Mines IC 7518 (1949).

54 ——— "Annual Report of Research and Technologic Work on Coal, Fiscal Year 1949." Bur. of Mines IC 7565 (1950).

55 Fieldner, A. C., and Rice, W. E. "Annual Report of Research and Technologic Work on Coal, Fiscal Year 1942." Bur. of Mines IC 7241 (1943).

56 Fieldner, A. C., et al. Bur. of Mines TP 601 (1939).

57 ——— Bur. of Mines TP 621 (1941).

58 Fosdick, A. H., and Underwood, C. E. "Coal Sizing and Coke Preparation (at Bethlehem)." *Bl. Furn. Coke Oven and Raw Matls. Comm.*, **6**, 23-37 (1947).

59 Foxwell, G. E. "The Path of Travel of the Gases in the Coke Oven." *Fuel*, **11**, 4-19 (1932).

60 —— "The Formation of Spongy Coke." *Gas World*, (Coking Sect.), **115**, 97-98 (1941); **116**, 4 (1942).

61 —— "The Shrinkage of Coke During Carbonization." *Coke Smokeless Fuel Age*, **3**, 76-80 (1941).

62 —— "Pressures Developed During Carbonization." *Coke and Gas*, **11**, 7-13 (1949).

63 Franklin, R. E. "A Note on the True Density, Chemical Composition, and Structure of Coals and Carbonized Coals." *Fuel*, **27**, 46-49 (1948).

64 —— "A Study of the Fine Structure of Carbonaceous Solids by Measurement of True and Apparent Densities. Part I. Coals." *Trans. Faraday Soc.*, **45**, 274-286 (1949).

65 —— "A Study of the Fine Structure of Carbonaceous Solids by Measurement of True and Apparent Densities. Part II. Carbonized Coals." *Ibid.*, **45**, 668-682 (1949).

66 Fuchs, W. "Thermodynamic Treatment of the Swelling Pressure of Coal." *J. Franklin Inst.*, **231**, 103-119 (1941).

67 —— "Processing of Swelling Coals for Use in By-Product Ovens." U.S. Pat. 2,341,861 (1944).

68 Fuchs, W., and Sandhoff, G. "Studies on Coking Pressure." *Fuel*, **21**, 70-73 (1942).

69 Fuchs, W., et. al. "Studies Concerning Pressure Developed During Carbonization of Coal." Penn. State Coll., Mineral Ind. Expt. Sta., Bull. 34 (1941).

70 Gauger, A. W. "The Composition and Properties of Fuels." Physical Chemistry and Technology of Fuels. 21st Ann. Priestly Lect., 1-41 (Penn. State College, 1947).

71 Gieseler, K. "The Expansion of Coal During Coking." *Gluckauf*, **77**, 309-319, 328-332 (1941).

72 Gillet, A. "The Carbonization of Coals and Their Geological Evolution." *Rev. Univ. Mines*, **89**, 145-155 (1946).

73 Gillet, A., and Dauvister, G. "Systematic Exploration of the Pyrolysis of a Coal Between 340 and 900°. III. Pyrolysis in a Current of Hydrogen." *Bull. soc. chim. Belg.*, **54**, 5-9 (1945); *Chem. Abs.*, **40**, 7563 (1946).

74 Gillet, A., and Koutcherenko, I. "New Experimental Investigation on the Transient Fusion of Coals." *Rev. Univ. Mines*, **5**, 338-351, 436-452 (1949).

75 Gillet, A., and Willeme, J. "Systematic Study of the Pyrolysis of Coal Between 340° and 900°. IV. Graduated and Comparative Pyrolysis of Coal. Evidence of the Relation of Coals." *Bull. soc. chim. Belg.*, **54**, 169-180 (1945); *Chem. Abs.*, **41**, 7703 (1947).

76 Gillet, A., Willeme, J., and Fastre, M. L. "Systematic Exploration of the Pyrolysis of a Coal Between 340° and 900°." *Bull. soc. chim. Belg.*, **53**, 27-44 (1944); *Chem. Abs.*, **40**, 4866 (1946).

77 Graham, J. P. Discussion in Ref. 168, which see.

77a Griffith, M., and Hirst, W. "The Heat of Wetting of Coals in Organic Liquids." Ultra-Fine Structure of Coals and Cokes. (BCURA, 1944).

78 Heuer, R. P., and Grigsby, C. E. "Proper Coke Oven Refractories Reduce Overhead Costs." *Steel*, **126**, No. 22, 65-68; No. 23, 98-100, 102, 104 (1950).

79 Hodsman, H. J. "Controlling Swelling in Carbonizing Bituminous Coal." Brit. Pat. 523, 250 (1940).

80 Horton, L., Randall, R. B., and Aubrey, K. V. "The Constitution of Coal. Summary of Existing Knowledge." *Fuel*, **23**, 65-80, 100-105 (1944).

81 Howard, H. C. "Low Temperature Reactions of Oxygen on Bituminous Coal." AIME TP 2233 (1947).

82 Isenberg, N., and Jackman, H. W. "Investigation of Beckley Seam Coal." (Inland Steel Co., 1945).

83 Jones, R. E., and Townend, D. T. A. "The Oxidation of Coal." *J. Soc. Chem. Ind.*, **68**, 197-201 (1949).

84 Kerr, H., and Taylor, A. "Some Factors Influencing the Life of Silica Coke Oven Batteries." *Gas World* (Coking Sect.), **129**, 117-132 (1948).

85 King, J. G. Wm. Young Memorial Lecture. *Gas World*, **130**, 1605-1610 (1949).

86 King, J. G., and Wilkins, E. T. "The Internal Structure of Coal." Ultra-Fine Structure of Coals and Cokes. (BCURA, 1944).

87 Koppers Co., Inc. "Coking of Expanding Coals." Brit. Pat. 630,128 (1949).

88 Koppers, H., and Jenkner, A. "The Bulk Density of Top-Charged Coal in Coke Ovens." *Fuel*, **9**, 521-526 (1930).

89 ——— "Determination of the Expansion Pressure Exerted in Laboratory and Large-Scale Coking Tests." *Ibid.*, **10**, 232-239, 273-277 (1931).

90 Kreulen, D. J. W. "Concerning the British Swelling Number of Coal." *Ibid.*, **29**, 112-117 (1950).

91 Krevelen, D. W. Van. "New Ideas on the Structure of Coal, Coalification, and Carbonization." *Chem. Weekblad*, **43**, 20-27 (1947); *Fuel Abs.*, **3**, No. 570 (1948).

92 Kruppa, W. J. "Coking Badly Swelling and Caking Coals." U.S. Pat. 2,336,151 (1943).

93 Kushnirevich, N. R. "Method of Determining the Expansion Pressure of Coals During the Coking Process." *Zavodskaya Lab.*, **13**, 325-328 (1947).

94 Landers, W. S., Schmidt, L. D., and Seymour, W. "Control of Bulk Densities in Coke Ovens; Studies on Coal Used at Three By-Product Coke Plants." Bur. of Mines RI 3807 (1945).

95 Lavine, I. and Gauger, A. W. "Studies in the Development of Dakota Lignite." *Ind. Eng. Chem.*, **22**, 1226-1234 (1930).

96 Lebedev, P. S. "Rapid Micro-Method for Determining Fusion Temperature and Coking Capacity of Bituminous Coals." *Zavodskaya Lab.* **9**, 326-332 (1940); *Chem. Abs.*, **36**, 2118 (1942).

97 —— "A New Explanation of Coke Formation." *Bull. acad. sci. URSS., Classe sci. tech.*, No. 3, 61-73 (1941); *Chem. Abs.*, **35**, 7685 (1941).

98 Lohr, F. D., and McGurl, G. V. "Regulating the Bulk Density of Coke-Oven Charges." U.S. Pat. 2,378,420 (1945).

99 Lowry, H. H. "Relation of the Physical Constitution of Coal to its Chemical Characteristics." *J. Geol.*, **50**, 357-384 (1942).

100 ——— "The Significance of the Chemical Nature of Coal." Carn. Inst. Tech., Coal Res. Lab., Contrib. 112 (1943).

101 ——— "Carbonaceous Products from Coal." *Chem. and Ind.*, 619-625, Aug. 19 (1950).

102 Lowry, H. H., editor, "Chemistry of Coal Utilization." (John Wiley and Sons, 1945).

103 Lowry, H. H., and Junge, C. O., Jr. "Significance of Criteria of Coal Plasticity." *Ind. Eng. Chem.*, **36**, 308-310 (1944).

104 Lowry, H. H., Landau, H. G., and Naugle, L. L. "Correlation of the BM-AGA Carbonization Assay Tests with Coal Analyses." AIME TP 1332 (1941).

105 Lowry, H. H., and Rose, H. J. "Coal and Coke Research, H. Koppers, G.m.b.H., Essen." Bur. of Mines IC 7422 (1947).

106 ——— "Fuel Research and Technology at Rheinisch-Westfalishes Kohlen-Syndicat, Essen." PB 4321.

107 ——— "Some Observations on German Coal Research and Developments." Bur. of Mines IC 7422 (1947).

108 McCartney, J. T., and Davis, J. D. "Expansion of Coal During Coking." Bur. of Mines RI 3644 (1942).

109 McCulloch, A. "Some Recent Conceptions of Coal Structure." *Can. Chem. and Proc. Ind.*, 1012-1016 (1947).

110 McKee, J. H. "Rate of Heating and the Carbonization and Intumescence of Coals." *Fuel*, **29**, 195-196 (1950).

111 Macura, H. "New Information Concerning the Behavior of Coal During Heating: Part I, The Softening Process." *Oel, Kohle, Erdoel, Teer*, **14**, 1097-1107 (1938); **15**, 1-12 (1939).

112 —— "Part II, Evolution of Volatile Matter." *Ibid.*, **15**, 45-54 (1939).

113 —— "Part III, Plasticization Behavior of Coal Mixtures." *Oel u. Kohle ver. Petroleum*, **36**, 117-121; 161-170 (1940).

114 —— "Part IV, Strength of Cokes from Blended Coals." *Oel u. Kohle*, **37**, 727-740 (1941).

115 ——— "Part V, The Relations Between Grinding Strength and Bending Strength of Coke." *Ibid.*, **39**, 113-116 (1943).

116 —— "Part VI, Shrinkage, Expansion and Coke Strength." *Ibid.*, **39**, 365-377 (1943).

117 —— "Part VII, Relations Among Shrinkage, Ash and Volatile Matter." *Ibid.*, **40**, 227-231 (1944).

118 —— "Part VIII, Caking Power and the Sintering Process." *Ibid.* **40**, 269-279 (1944).

119 Maggs, F. A. P. "The Relation Between Heat of Wetting and the Absolute Value of the Surface Area of Coals." *J. Inst. Fuel*, **17**, 49-54 (1943).

120 —— "Adsorption of Vapors on Carbonized Coal." Ultra-Fine Structure of Coals and Cokes. (BCURA, 1944).

121 —— "Assessment of Specific Surface of Powders and Porous Solids by Adsorption Methods." *BCURA Bull.* **9**, 253-261 (1945).

122 —— "Adsorption Swelling of Several Carbonaceous Solids." *Trans. Faraday Soc.*, **42B**, 284-288 (1946).

123 Mainz, H., and Schwarzmann, H. "Swelling Properties of Coal." *Gluckauf*, **81/84**, 452-458 (1948).

124 Mayers, M. A., and Thompson, J. A. "A Carbonization Pressure Gage." *Trans. AIME*, 271-280 (1944).

125 Mott, R. A. "Coal Assessment." *J. Inst. Fuel*, **22**, 2-11 (1948).

126 —— "Laboratory Assays for the Selection of Coking Coals." *Gas World* (Coking Sect.) **130**, 91-99 (1949).

127 —— "Studies in Coke Formation." *Fuel*, **12**, 185-194, 412-418 (1933).

128 —— "Coals Dangerous to Coke Ovens." *J. Inst. Fuel*, **13**, 189-200, 257-264 (1940).

129 —— "The Caking and Swelling Power of Coal." *Fuel*, **21**, 51-62, 80-88 (1942).

130 Mott, R. A., and Spooner, C. E. "The Shrinking Power of Coke." *Gas World* (Coking Sect.), **114**, 31-33 (1941).

131 ——— "Studies in Coke Formation." *Fuel*, **16**, 4-14 (1937).

132 ——— "The Assessment of Coals Liable to Damage Oven Walls." *Fuel*, **18**, 329-344, 371-379 (1939).

133 Mulcahy, B. P. "Selection of Coal for Carbonization." *Trans. AIME*, **157**, 251-270 (1944).

134 Naugle, B. W., et. al. "Measurement of Coking Pressure in a Small Laboratory Oven." Bur. Mines RI 4285 (1948).

135 Naugle, B. W., Davis, J. D., and Wilson, J. E. (Bureau of Mines). "Precision of Expansion Tests on Coal and Relation of Expansion to Other Variables." Presented at Div. of Gas and Fuel Chem., Amer. Chem. Soc., Chicago, Sept. 4, 1950.

136 Nikolskii, N. A., and Stepanenko, M. A. "Direction of Tar Vapors and Gases Inside of the Charge During Coking." *Khim. Tverd. Topliva*, **9**, 28-42 (1938).

137 Onusaitis, B. A., and Yurevskaya, N. P. "Formation of Microstructure of Coke." *Bull. acad. sci. URSS, Classe sci. tech.*, 881-894 (1947); *Chem. Abs.*, **43**, 4834 (1949); *Fuel Abs.* (N.S.) **3**, No. 3, 19 (1948).

138 Otto, C. "Coking Expanding Coal." U.S. Pat. 2,382,809 (1945).

139 Parks, B. C., and O'Donnell, H. J. "Determination of Petrographic Components of Coal by Examination of Thin Sections." AIME TP 2492 (1948).

139a Parry, V. F., "Production, Classification, and Utilization of Western United States Coals." *Ec. Geol.*, **45**, 515-532 (1950).

140 Perch, M. "Coking Expanding Coals." U.S. Pat. 2,504,150 (1950).

141 Perch, M., and Russell, C. C. "A Study of Coal Classification and Its Application to the Coking Properties of Coal." *Min. Eng. (Min. Trans.)*, **184**, 205-214 (1949); AIME TP 2584 F (1949).

142 Perry, J. H. "Chemical Engineers Handbook." p. 1540 (McGraw-Hill, 1941).

143 Pettyjohn, E. S., Ball, W. E., and Brysch, O. P. "Bulk Density Control of Coal Charged to Ovens." Presented at Chicago District Bl. Furn. and Coke Oven Assn., March 3, 1950.

144 Pontypridd Test Plant Committee. "A Study of the Pressures Developed by British Coals During Carbonization." TP No. 2 (BCRA, 1948).

145 Porter, H. C. "Reduction of Expansion Pressure by Oxidation of Coal." U.S. Pat. 2,359,581 (1944).

146 Porter, H. C., and Ralston, O. C. "Some Properties of the Water in Coal." Bur. Mines. TP 113 (1916).

147 Powell, A. R. "Coking Process." U.S. Pat. 2,495,763 (1950).

148 Puening, F. "Method and Apparatus for Preparing Coal for Coking." U.S. Pat. 2,408,810 (1946).

149 Puening, F., and Bower, A. L. "Sealing Device for Coke Oven with Movable Walls." U.S. Pat. 2,490,090 (1949).

150 Ramsburg, C. J., and McGurl, G. V. "Carbonization of Coal-Oil Mixtures." *AGA Proc.*, 666-681 (1940). *Am. Gas J.*, **153**, No. 5, 59-64 (1940).

151 Reed, F. H., et. al. "Use of Illinois Coal for Production of Metallurgical Coke." Ill. State Geol. Surv. Bull. 71 (1947).

152 Rees, O. W., Land, G. W., and Reed, F. H. "Moisture Relations of Banded Ingredients in an Illinois Coal." *Ind. Eng. Chem.*, **33**, 416-419 (1941).

153 Rees, O. W., Wagner, W. F., and Tilbury, W. G. "Chemical Characteristics of Banded Ingredients of Coal." *Ibid.*, **39**, 1516-1520 (1947).

154 Reuter, F. "Use of the Hessler Carbonization Test Apparatus for Determining Coal Characteristics." *Gas-u. Wasserfach*, **91**, 137-139 (1950).

155 Reynolds, D. A., and Holmes, C. R. "Procedure and Apparatus for Determining Carbonizing Properties of American Coals by the BM-AGA Method." U.S. Bur. Mines, TP 685 (1946).

156 Reynolds, D. A., and Birge, G. W. "Coal Carbonization: Gas Pressure Within the Uncarbonized Part of a Charge." *Ind. Eng. Chem.*, **32**, 363-367 (1940).

157 Riley, H. L. "X-Ray Crystallography of Bituminous Coal." 11th Int. Congr. Pure and Appl. Chem., London, July 17-24, (1947); discussion, *Gas World*, **127**, 166 (1947).

158 Roberts, J. "Swelling Pressures in Coke Ovens." *Coke Smokeless-Fuel Age*, **3**, 128-129 (1941).

159 Roga, B. "Improvement of Coke Quality in Poland." *Gas World* (Coking Sect.), **132**, 77-81 (1950).

160 Roller, P. S. "Law of Size Distribution and Statistical Description of Particulate Material." *J. Franklin Inst.*, **223**, 609-633; (p. 60, "Micrometretics," J. M. Dallavalle, 1948).

160a Rose, H. J., "Selection of Coals for the Manufacture of Coke." *AIME Trans.*, **74**, 600-639 (1926).

161 Rühl, G. "Lowering the Working Pressure of Coal." Ger. Pat. 729,057 (Nov. 12, 1942); *Chem. Abs.*, **38**, 471 (1944).

162 Russell, C. C. "Measurement of Pressures Developed During the Carbonization of Coal." *Trans. AIME*, **139**, 313-327 (1940); AIME TP 1118 (1939); *Gas J.*, **232**, 424, 427-428 (1940).

163 —— "Practical Significance of Coal Expansion Tests." Presented at Joint Prod. and Chem. Conf., AGA, New York, May 23 (1938).

164 —— "Subcommittee XV on Plasticity and Swelling, ASTM Committee D-5." *Proc. ASTM* (1949).

165 —— "Selection of Coals for the Manufacture of Coke." *AGA Proc.*, 733-756 (1947).

166 Russell, C. C., and Perch, M. "Some Physical Characteristics of By-Product Coke for Blast Furnaces." AIME TP 1520 (1942).

167 ——— "Studies of the Plastic Properties of Coal as Related to Coal Carbonization." *AGA, Report of Gas Production Committee*, p. 6-23 (1949).

168 Russell, C. C., Perch, M., and Farnsworth, J. F. "Reducing Coal Expansion Pressure." *Proc. Bl. Furn., Coke Oven, and Raw Matls. Conf., AIME*, (1949).

169 Ryan, W. P. "Rate of Travel of Fusion Zone in Coke Ovens." *AGA Proc.*, 861-878 (1925).

170 Sapozhnikov, L. M. "The Mechanism of Coking Bituminous Coals and Their Mixtures." *Coke Smokeless-Fuel Age*, **1**, 27-31, 58-59 (1939).

171 —— "A Theory of the Formation of Blast Furnace Coke." *Bull. acad. sci. URSS, Classe sci. tech.*, No. 4, 3-26 (1941).

172 Sapozhnikov, L. M., and Cherkasskaya, E. I. "Plastometric Coordinates and the Course of Gas Evolution." *Khim. Tverd. Topliva*, **6**, No. 1, 28-33 (1935).

173 Sapozhnikov, L. M., and Taits, E. M. "A New Method for the Characterization of Agglomerated Coals." *Bull. acad. sci. URSS, Classe sci. tech.*, No. 10, 5-8 (1939); *Chem. Abs.*, **36**, 6777 (1942).

174 Savage, P. S. "The Blending of Coals to Improve Coke and Extend Coking Coal Reserves." *Bl. Furn. and Steel Plant*, **37**, 323-324, 334 (1949).

175 Schmidt, L. D. "Effects of Storage and Oxidation of Coal Upon Coking Properties." *Iron and Steel Engr.*, **18**, No. 3, 64-70, 70-72 (1941).

176 Schmidt, L. D., Elder, J. L., and Davis, J. D. "Influence of Storage on Caking and Coking Properties of Coal." *Ind. Eng. Chem.*, **33**, 150-155 (1943).

177 ——— "Atmospheric Oxidation of Coals at Moderate Temperature. Effect of Oxidation on the Carbonizing Properties of Representative Coking Coals." *Ibid.*, **32**, 548-555 (1940).

178 Schmidt, T. "The Coking Process and the Path of Travel of the Gases in the Coke Oven." *Fuel*, **5**, 486-509 (1926).

178a Selvig, W. A., and Ode, W. H. "An Investigation of a Laboratory Test for Determination of the Free-Swelling Index of Coal." Bur. Mines RI 4238 (1948).

179 Seyler, C. A. "Notes on the Softening of Coal." *J. Inst. Fuel*, **14**, 195-196 (1941); *Chem. Abs.*, **35**, 8247 (1941).

180 Seyler, C. A., and Edwards, W. J. "Technique of Coal Petrography." *Fuel*, **28**, 121-127 (1949).

181 Seymour, W., and Schmidt, L. D. "Control of Bulk Density of the Coal Charge in By-Product Coke Ovens." Bur. Mines RI 3743 (1943).

182 Shnidman, L. "Ash Structure in Coke." *Ind. Eng. Chem.*, **35**, 1262-1263 (1943).

183 Shotts, R. Q. "The Relation of Free-Swelling Indexes to Other Characteristics of Some Alabama Domestic Stoker Coals." AIME TP 2314 (1948).

184 Soth, G. C., and Russell, C. C. "The Gieseler Method for Measurement of the Plastic Characteristics of Coal." *Proc. ASTM*, **43**, 1176-1189 (1943).

185 ——— "Sources of Pressure Occurring During Carbonization of Coal." *Trans. AIME*, **157**, 281-305 (1944).

186 South Metropolitan Gas Company. "The Moisture Sorption of Coals and Its Relation to Their Coking Quality." *Fuel*, **25**, 42-50 (1946).

187 Spooner, C. E., "The Significance of the Ultimate Analysis of Coal." *J. Inst. Fuel*, **17**, 161-162 (1944).

188 Sprunk, G. C., et. al. "Splint Coals of the Appalachian Region: Their Occurrence, Petrography, and Comparison of Chemical and Physical Properties With Associated Bright Coals." Bur. of Mines TP 615 (1940).

189 Studemund, W. "Coal Carbonization in the Light of Recent Research." *Gas-u. Wasserfach*, **87**, 37-41 (1944).

190 Swietoslawski, W. "Coke Formation Process and Physico-Chemical Properties of Coals." (Polish Inst. of Arts and Sciences in America, 1942).

191 Swiniarski, J. H., Cryan, M. C., and Altieri, V. J. "Selection of Coals for War Time Carbonization by Means of an Improved Engineering Model of the Coke Oven." *AGA Proc.*, **24**, 414-416 (1942); *Gas Age*, **89**, No. 13, 14-15 (1942).

192 Taits, E. M. "Rapid Method for Determining the Caking Capacity of Coals." *Zavodskaya Lab.*, **10**, 514-516 (1941); *Chem. Abs.*, **35**, 8249 (1941).

193 —— "Application of the I.G.I. Method for Determining the Coking Power of Coal." *Bull. acad. sci. URSS*, No. 10-11, 773-783 (1944); *BCURA Bull.*, No. 899 (1946).

194 Taits, E. M., Samoilovich, P. Y., and Strongin. "Determination of the Caking Tendency of Kuznetsk Basin Coal." *Ugol*, **20**, No. ½, 10-14 (1945); *Chem. Abs.*, **40**, 1644 (1946).

195 Taylor, J. "The Swelling Pressure of Coal and the Formation of Spongy Coke." *Fuel*, **10**, 390-393 (1931).

196 Thiessen, R., and Sprunk, G. C. "The Effect of Heat on Coal as Revealed by the Microscope." *Fuel*, **13**, 116-125 (1934).

197 Townend, F. S., and Spiers, H. M. "The Examination of Coal as a Guide to Coke-Oven Projects." *Gas World* (Coking Sect.), **118**, 15-22 (1943).

198 Ulrich, F. "Determination of the Expansion Pressure of a Coal in the Oven Chamber." *Glückauf*, **75**, 128-133 (1939).

199 Ussar, M. "The Swelling of Bituminous Coals." *Berg. u. huttenmann, Monatsch.*, **94**, 103-108 (1949).

199a Veit, P. "Carbonizing Period in Coke Ovens." *Brennstoff Chem.*, **31**, 14-22 (1950).

200 Weed, R. C. "Metallurgical Tests for Control of Coal and Coke Quality." Bl. Furn., Coke Oven and Raw Matls. Conf., Apr. 10-12 (1950).

201 Wilputte Coke Oven Division. "Coal Testing Oven." (1949).

202 Wilson, D. W. "Mechanism of High Temperature Coal Carbonization." *AGA Proc.*, 952-964 (1923).

203 Wilson, P. J., and Wells, J. H. "Coal, Coke and Coal Chemicals." (McGraw-Hill, 1950).

204 Wolf, C. S. "Acid Treatment of Coking Coals." Can. Pat. 405, 754, (June 30, 1942); *Chem. Abs.*, **36**, 5637 (1942).

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